OL

46

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : A01N 25/32 | A1 | (11) International Publication Number: WO 92/11761
(43) International Publication Date: 23 July 1992 (23.07.92)

(21) International Application Number: PCT/US91/09783

(22) International Filing Date: 30 December 1991 (30.12.91)

(30) Priority data:
636,360 31 December 1990 (31.12.90) US
808,590 20 December 1991 (20.12.91) US

(60) Parent Application or Grant
(63) Related by Continuation
US 636,360 (CIP)
Filed on 31 December 1990 (31.12.90)

(71) Applicant *(for all designated States except US):* MONSANTO COMPANY [US/US]; 800 North Lindbergh Boulevard, St. Louis, MO 63167 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)* : BUSSLER, Brett, Hayden [US/US]; 2631 Inglewood Avenue, St. Louis Park, MN 55416 (US). HAKES, Harrison, Ross [US/US]; 421 Downhill Drive, Ballwin, MO 63021 (US). MAYONADO, David, James [US/US]; 15611 Parasol Drive, Chesterfield, MO 63017 (US).

(74) Agent: BOLDING, James, Clifton; Monsanto Company, 800 North Lindbergh Boulevard, St. Louis, MO 63167 (US).

(81) Designated States: AT (European patent), AU, BE (European patent), BG, BR, CA, CH (European patent), CS, DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GB (European patent), GR (European patent), HU, IT (European patent), JP, KR, LU (European patent), MC (European patent), NL (European patent), PL, RO, RU ,SE (European patent), US.

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: REDUCING PESTICIDAL INTERACTIONS IN CROPS

(57) Abstract

The disclosure herein relates to means for combatting the adverse phytotoxic action to crops arising from the interaction of various herbicidal compounds and biocidal compounds, e.g., insecticidal and/or fungicidal compounds. The means employed to reduce said interaction involves the safening action of various antidotal compounds.

REDUCING PESTICIDAL INTERACTIONS IN CROPS

FIELD OF THE INVENTION

The field of the invention contemplated herein pertains to the safening of enhanced herbicidal phytotoxicity induced by the interaction with various biocides, especially insecticides. The safening action is effected by the presence of various antidotal (safener) compounds.

BACKGROUND OF THE INVENTION

It is a common practice in agricultural practice to apply herbicidal compositions to control undesirable vegetation in cultivated crops. Such herbicidal compositions may contain other additaments such as fertilizers, biocides, e.g., insecticides, fungicides, nematicides, etc., herbicide antidotes, etc.

Additional agricultural practices include the application of said herbicidal compositions to soils or vegetation previously treated with said biocides. However, a long history of experience with focused attention developing in the early 1960s has shown that major problems can arise as a result of the interaction of herbicides and various biocides, particularly various insecticides and/or fungicides. The common result of such interaction is the enhancement of the phytoxic activity of the herbicide in various crops. This enhanced phytotoxicity is referred to in the literature and will be so used herein as "negative synergy/synergism" between the herbicide(s) and the biocide(s). Such negative synergism is expressed in terms or decreased emergence of a crop, reduced crop survival or vigor, crop stand reduction and/or crop yield.

The herbicides and biocides giving rise to negative synergy when in contact with each other have been found to include members from a variety of classes, including, but not limited to, in the case of herbicides, sulfonylureas, imidazolinones, aliphatic and aromatic carboxylic acids, amides salts and esters, is xaz lidinones, ureas, triazines, thi carbamates,

bserved significant interacti ns between the pesticides, with many combinations of pesticides giving a variety of negative synergistic effects, including reduction in seedling emergence, significant reduced cotton seedling survival and/or vigor and/or stand reduction and/or yield.

Reports by H. W. Ivy et al in Proc. SWSS, p. 94, 1969 and p. 132, 1973 cite a variety of pesticide interactions with the same herbicides used by Chambers et al; chloroneb or PCNB with or without Terrazole fungicides and phorate, disulfoton and UC-21149 (aldecarb) insecticides. Various combinations resulted in negative synergism in cotton.

In Proc. SWSS-95, 1969, B. J. Johnson reported negative synergism in terms of significantly reduced seedling vigor in soybeans due to the interaction of various combinations of Amiben ethyl ester, trifluralin and linuron herbicides and methomyl and phorate insecticides.

R. M. Hayes et al reported that use of non-recommended rates of the herbicide metribuzin and the insecticides disulfoton and phorate resulted in significant reductions in yield and stand reductions of two varieties of soybeans. Proc. SWSS-1976 p. 95.

More recently, C. D. Applewhite reported (Proc. SWSS, p. 83, 1990) on tests in cotton with various application modes (granular in-furrow or tank spray) of clomazone with and without fluometuron herbicides in combination with the OP insecticides disulfoton, phorate, aldecarb and acephate and the nematicide fenamiphos. A number of combinations of these chemicals and application modes gave a variety of responses ranging from the safening of clomazone by the interaction of disulfoton and phorate applied in-furrow as granular formulations, but accompanied by some plant discolorati n and a 7% stand reduction; no effect on safening by f namiphos, but producing the same plant discolorati n and stand reduction as the OP

c ntrol tr ubles me insects." (Underlines in cited document).

In an article in the Canadian Journal of Plant Science, Vol. 58, pp. 1119-1121 (Oct., 1978), numerous citations are made to studies resulting in findings of negative synergism between various herbicides and insecticides in various crops, including corn injury by the interaction of Eradicane and fonofos.

In the study reported in said article, the authors evaluated the effect on corn of applications of the insecticide fonofos on the herbicides EPTC and vernolate containing the antidote dichlormid (i.e., Eradicane and Surpass, respectively). In tests in succeeding years (1976 and 1977) the authors found no negative synergy between fonofos and the herbicides containing the antidote in 1976, but in 1977 found severe damage to corn ear quality and reduction in tiller numbers, albeit insignificant, by Eradicane plus fonofos. The 1977 results confirmed reports by some growers in 1975. No negative synergy was found between the Surpass plus fonofos treatments in either of the two-year trials.

The authors concluded that negative synergy with these herbicides and fonofos in corn can be inconsistent from year to year, possibly because of soil and weather conditions. It is noteworthy that the authors did not even discuss, much less recognize, any significance in the presence of the antidote dichlormid - which in their 1977 tests did not prevent corn injury. Nor did the authors comment on the fact that the particular combination of vernolate plus dichlormid caused no injury to corn, with or without fonophos, an inference, therefore, that vernolate and fonophos may not induce negative synergism.

On the other hand, in tests with fonofos and other soil-insecticides, e.g., terbufos, chlorpyrifos and thimet, with another herbicide, the sulfonylurea

biocides, even th ugh such other herbicides, e.g., acetamid s, thiocarbamates, etc., are not known to be ALS inhibitors, but do exhibit a similar mode of inhibitory action.

SUMMARY OF THE INVENTION

In one aspect, the present invention relates to compositions comprising: (a) a herbicidal component; (b) a biocidal component and (c) an antidotal component, which latter component inhibits, reduces or prevents the tendency to interact or the actual interaction of the former two components to enhance the phytotoxicity of said herbicidal component. Such enhanced phytotoxicity is defined as "negative synergy or synergism".

In another aspect, this invention relates to a method for combatting, inhibiting, reducing or preventing negative synergism resulting from the interaction of herbicidal and biocidal compounds by use of an antidotal compound.

In preferred embodiments, the herbicidal component is a compound which causes an ALS inhibition reaction in plants. By "ALS inhibition" is meant that the effect of the herbicide on the plant is to interrupt or inhibit the aceto lactate synthase ("ALS") enzyme in the amino acid pathway leading to plant proteins. Compounds known to exhibit such ALS inhibitory reaction in plants include sulfonylureas, imidazolinones and azolopyrimidine sulfonamides.

Other herbicidal compounds which cause negative synergy, either through an ALS or non-ALS or some other form of inhibitory action in weed plants include α-haloacetamides, thiocarbamates, aliphatic and aromatic carboxylic acids, amides, salts and esters, isoxazolidinones, ureas, triazines, nitrobenzenes, etc.

In more particular, preferred herbicidal compounds useful in the present invention are selected fr m az lopyrimidine sulf namide, sulf nylurea, imida-

haloalkyl, alkylthio, alk xy, alk xyalkyl, amino, m no- or di-C_{1-4} alkylamino, phenyl or an R_3 phenyl-substituted member;

R_4 and R_6 are independently H or alkyl, acyl, alkenyl, alkenyloxy, alkenyloxycarbonyl, alkynyl, alkynyloxy, alkanoyl, alkoxy, haloalkoxy, haloalkylthio, alkoxyalkyl, alkoxycarbonyl, or alkoxythiocarbonyl, each having up to 10 carbon atoms; phenyl, benzyl, naphthyl-phenylthio, phenoxy, phenoxythio, phenoxycarbonyl, phenyl $S(O)_n$; phenyl $S(O)_nC_{1-4}$ alkyl; phenyl $S(O)_nC_m(K)_{2m}H$; phenyl $S(O)_nCK_3$, where n is 0, 1, 2 or 3, m is 1-3 and K is halogen; phenoxy- carbonyl, phenoxythiocarbonyl, aminocarbonyl, or where not self-inclusive said R_4 and R_6 members substituted with halogen, CN, CF_3, NO_2, OH and/or C_{1-10} alkyl, haloalkyl, alkoxy, alkoxy- alkoxy, hydroxyalkoxy, alkylthioalkoxy, alkoxycarbonyl, or polyalkoxycarbonyl, phenyl, halophenyl, benzyl, benzyloxy, phenoxyalkoxy and agriculturally-acceptable salts thereof when R_4 and R_6 are H and

R_5 and R_7 are independently an aromatic hydrocarbon or heterocyclic radical having up to 10 ring members of which up to four may be N, O and/or S in the heterocyclic radical and said R_5 and R_7 members sub-stituted with one or more R_4 members, 2-pyridyl, 2-pyridyloxy or 2-pyridylmethoxycarbonyl, dialkyl-aminoalkoxycarbonyl having up to 10 carbon atoms and the radical $C(O)ON = C(R_9)_2$, wherein R_9 is H, phenyl, phenyl-carbonyl, benzyl, C_{1-10} alkyl, alkoxy, mono- or di-C_{1-6} alkylamino or -alkylaminocarbonyl, $-S(O)_nR_{10}$, where n is 0, 1, 2 or 3 and R_{10} is C_{1-6} alkyl, haloalkyl, mono- or di-C_{1-4} alkylamino or alkylcarbonyl, said compound of Formula I being used alone or in admixture with other known herbicidal compounds as co-herbicides, preferably an α-haloacetamide as defined hereinafter.

Preferred herbicidal compounds according to Formula I are thos wherein A and B are both nitrogen; R is $-SO_2N(R_6)(R_7)$; R_1 is phenyl, pyrimidinyl, triazinyl, thiadiazolyl, pyrazinyl, pyridinyl, or any of said R_1

5-(2,5-dimethylpyrrol-1-yl)-1,2,4-triazole-3-sulphonamide; N-(2,6-difluorophenyl)-5-(2,5-dimethylpyrrol-1-yl)-1,2,4-triazole-3-sulphonamide; N-(2,6-dichloro-3-methyl-phenyl)-1-(4,6-dimethylpyrimidin-2-yl)-1,2,4-triazole-3-sulphonamide; N-(2,6-dichlorophenyl)-5-amino-1-(4,6-dimethylpyrimidin-2-yl)-1,2,4-triazole-3-sulphonamide; or N-(2,6-dichloro-3-methylphenyl)-5-amino-1-(4,6-dimethoxy-1,3,5-triazin-2-yl)-1,2,4-triazole-3-sulphonamide.

In other embodiments of the invention, more preferred herbicidal compounds according to Formula I are those wherein A and B are both nitrogen (N), R is $-SO_2N(R_6)(R_7)$ and R_1 and R_2 are combined to form one of the following divalent radicals:

(a) $$-N=\overset{\overset{Z}{|}}{C}-\overset{\overset{Y}{|}}{C}=\overset{\overset{X}{|}}{C}-$$

(b) $$-NH-\overset{\overset{Z}{|}}{CH}-\overset{\overset{Y}{|}}{CH}-\overset{\overset{X}{|}}{CH}-$$

(c) $$-NH-\overset{\overset{Z}{|}}{C}=\overset{\overset{Y}{|}}{C}-\overset{\overset{X}{|}}{CH}-$$

(d) $$-N=\overset{\overset{Z}{|}}{C}-\overset{\overset{Y}{|}}{CH}-\overset{\overset{X}{|}}{CH}-$$

(e) $$-\overset{\overset{Z}{|}}{C}=\overset{\overset{Y}{|}}{C}-N=\overset{\overset{X}{|}}{C}-$$

(f) $$-N=\overset{\overset{Y}{|}}{C}-\overset{\overset{X}{|}}{N}-\overset{\overset{D}{\|}}{C}-$$

(g) $$-S-\overset{\overset{Y}{|}}{C}=\overset{\overset{X}{|}}{C}-$$

5-methyl-N-(2,6-difluoro-3-methylphenyl)-1,2,4-triazolo-[1,5-a]-pyrimidine-2-sulfonamide;

5-methyl-N-(2,6-difluorophenyl)-1,2,4-triazolo[1,5-a]-pyrimidine-2-sulfonamide;

5,7-dimethoxy-N-(2,6-dichloro-3-methylphenyl)-1,2,4-triazolo-[1,5-a]-pyrimidine-2-sulfonamide;

5,7-dimethoxy-N-(2-methoxy-6-trifluoromethyl-phenyl)-1,2,4-triazolo-[1,5-a]-pyrimidine-2-sulfonamide;

5-methyl-7-methylthio-N-(2,6-dichlorophenyl)-1,2,4-triazolo-[1,5-a]-pyrimidine-2-sulfonamide;

5-methyl-7-methylthio-N-(2-trifluoromethylphenyl)-1,2,4-triazolo-[1,5-a]-pyrimidine-2-sulfonamide;

7-ethoxy-5-methyl-N-(2,6-dichloro-3-methylphenyl)-1,2,4-triazolo-[1,5-a]pyrimidine-2-sulfonamide;

5,7-dimethyl-N-(2-chloro-6-phenylphenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide;

5-methyl-N-(2-methyl-6-nitrophenyl)-1,2,4-triazolo[1,5-a]-pyrimidine-2-sulfonamide;

5-methyl-N-(2-chloro-6-methylphenyl)-1,2,4-triazolo[1,5-a]-pyrimidine-2-sulfonamide;

Methyl-3-methyl-N-(5,7-dimethyl-1,2,4-triazolo-[1,5-a]-pyrimidine-2-sulfonyl)anthranilate;

Methyl-3-methyl-N-(5-methyl-7-ethoxy-1,2,4-triazolo-[1,5-a]-pyrimidine-2-sulfonyl)-anthranilate;

Isopropyl-3-methyl-N-(5-methyl-1,2,4-triazolo-[1,5-a]-pyrimidine-2-sulfonyl)anthranilate;

6-Methyl-N-(2-bromo-6-methylphenyl)-1,2,4-triazolo-[1,5-a]-pyrimidine-2-sulfonamide;

6-Methyl-N-(2-fluoro-6-chlorophenyl)-1,2,4-triazolo-[1,5-a]-pyrimidine-2-sulfonamide;

6-Methyl-N-(2-chloro-6-methylphenyl)-1,2,4-triazolo[1,5-a]-pyrimidine-2-sulfonamide;

6-Methyl-N-(2-methyl-6-nitrophenyl)-1,2,4-triaz lo-[1,5-a]-pyrimidine-2-sulfonamide;

5-Methyl-7-ethoxy-N-(2-chloro-1-naphthyl)-1,2,4-triazolo-[1,5-a]-pyrimidine-2-sulfonamide;

5-Methyl-N-(2-methylpropanoyl)-N-(2,6-difluorophenyl)-1,2,4-triazolo-[1,5-a]-pyrimidine-2-sulfonamide;

5-Methyl-N-acetyl-N-(2,6-dichlorophenyl)-1,2,4-triazolo-[1,5-a]-pyrimidine-2-sulfonamide;

5,7-Dimethyl-2-(N-[2-chloro, 6-propargyloxyphenyl]-sulphamoyl)-1,2,4-triazolo[1,5-a]-pyrimidine;

5,7-Dimethyl-2-(N-[2-chloro-6-(2-ethoxyethoxy)-phenyl]-sulphamoyl)-1,2,4-triazolo[1,5-a]-pyrimidine;

5,7-Dimethyl-2-(N-[2-benzyloxy-6-chlorophenyl]-sulphamoyl)-1,2,4-triazolo[1,5-a]-pyrimidine;

5,7-Dimethyl-2-(N-[2-allyloxy-6-fluorophenyl]-sulphamoyl)-1,2,4-triazolo[1,5-a]-pyrimidine;

5,7-Dimethyl-2-(N-[2-chloro-6-(2-methoxymethoxy)-phenyl]-sulphamoyl)-1,2,4-triazolo[1,5-a]-pyrimidine;

5,7-Dimethyl-2-(N-[2-chloro-6-(2-hydroxyethoxy)-phenyl]-sulphamoyl)-1,2,4-triazolo[1,5-a]-pyrimidine;

5,7-Dimethyl-2-(N-[2-2-ethoxyethoxy)-6-fluoro-phenyl]-sulphamoyl)-1,2,4-triazolo[1,5-a]-pyrimidine;

5,7-Dimethyl-2-(N-[2-fluoro-6-(2-methylthio-ethoxy)-phenyl]-sulphamoyl)-1,2,4-triazolo-[1,5-a]-pyrimidine;

5,7-Dimethyl-2-(N-[2-chloro-6-(2-phenoxyethoxy)-phenyl]sulphamoyl)-1,2,4-triazolo[1,5-a]-pyrimidine;

5,7-Dimethyl-2-(N-[2-chloro-6-(2-methoxyethoxy)-phenyl]-sulphamoyl-1,2,4-triazolo-[1,5-a]-pyrimidine;

5,7-Dimethyl-2-(N-[2-chloro-6-(2-n-propoxyethoxy)-phenyl]-sulpham yl)-1,2,4-triazolo[1,5-a]-pyrimidine;

Other preferred herbicidal comp unds for use herein wherein in Formula I R_1 and R_2 are combined to form divalent radical (a) above, i.e.,

$$\text{(a)} \qquad -N=\overset{\displaystyle Z}{\overset{|}{C}}-\overset{\displaystyle Y}{\overset{|}{C}}=\overset{\displaystyle X}{\overset{|}{C}}-$$

and R is $-SO_2N(R_6)(R_7)$, are those wherein A is CR_3, B is N and R_6, R_7, X, Y and Z have the above-defined meanings and

R_3 is H, halogen, NO_2, CN, amino, phenyl, phenylthio, phenoxy, C_{1-4} alkyl, mono- or di-C_{1-4} alkyl-amino or alkoxy; $-S(O)_{0-3}-C_{1-4}$ alkyl; $C(O)C_{1-4}$ alkyl, -alkoxy, -alkylthio, mono- or dialkylamino or -phenyl; or a substitutable R_3 member substituted where not self-inclusive with halogen, NO_2, CN, CF_3 and/or C_{1-3} alkyl, preferably methyl.

Preferred compounds according to the foregoing embodiment are those wherein:

X and Z are independently H, CN, halogen, amino, C_{1-4} alkyl, haloalkyl, alkylthio, alkoxy or mono- or dialkylamino;

Y is H, CN, halogen, C_{1-4} alkyl, haloalkyl or alkoxy;

R_3 is halogen, NO_2, CN, C_{1-4} alkyl, haloalkyl, C(O)alkyl or C(O)alkoxy;

R_6 is H, benzyl, $C(O)C_{1-4}$alkyl or -haloalkyl and agriculturally-acceptable salts thereof when R_6 is H and

R_7 is phenyl substituted in at least one ortho position with halogen, CN, NO_2, C_{1-4} alkyl, haloalkyl or $S(O)_{1-3}$alkyl or haloalkyl; amino, mono- or di-C_{1-4}alkylamino, optionally substituted phenyl, phenylthio, phenoxy or benzyl, wherein said substituents are from 1 to 4 of halogen, NO_2, CF_3, CN or C_{1-3} alkyl, preferably methyl; and at least one of the meta positions of the R_7 phenyl group is substituted with a C_{1-3} alkyl, preferably methyl.

Preferred and representative herbicidal compounds according to Formula I wherein R_1 and R_2 are combined to form the bivalent radicals (c) and (d) above include tautomeric forms of the following compounds:

5,7-Dimethyl-N-(2-chloro-6-methylphenyl)-1,2,4-triazolo-[1,5-a]-[4H,7H]-dihydropyrimidine-2-sulphonamide,

7-Methyl-N-(2-chloro-6-methylphenyl)-1,2,4-triazolo-[1,5-a][4H,7H]-dihydropyrimidine-2-sulphonamide;

5,7-Dimethyl-N-(2-chloro-6-ethoxyphenyl)-1,2,4-triazolo-[1,5-a][4H,7H]-dihydropyrimidine-2-sulphonamide or

5,7-Dimethyl-N-(2-chloro-6-isopropoxyphenyl)-1,2,4-triazolo-[1,5-a][4H,7H]-dihydropyrimidine-2-sulphonamide.

Another group of preferred herbicidal compounds of Formula I are those wherein R_1 and R_2 combine to form the divalent radical (e) above, i.e.,

$$(e)\qquad -\overset{Z}{\overset{|}{C}} = \overset{Y}{\overset{|}{C}} - N = \overset{X}{\overset{|}{C}} -$$

wherein

X is H, CF_3, C_{1-4} alkyl, alkylthio or alkoxy;

Y and Z are independently H, CF_3, CF_3, halogen or C_{1-4} alkoxy; provided that at least one of X, Y or Z is C_{1-4} alkoxy;

R_6 is H or $C(O)C_{1-4}$ alkyl or -haloalkyl and agriculturally-acceptable salts thereof when R_6 is H and

R_7 is phenyl substituted in at least one ortho position with halogen, CN, NO_2, C_{1-4} alkyl, haloalkyl or $S(O)_{1-3}$ alkyl or haloalkyl; amino, mono- or di-C_{1-4} alkylamino, optionally-substituted phenyl, phenylthio, phenoxy or benzyl, wherein said substituents are from 1 to 4 of halog n, NO_2, CF_3, CN r C_{1-3} alkyl, pref rably methyl; and at least one of the m ta p si-

alkyl, alkenyl or alkynyl having up to 6 carbons, which may optionally be substituted with one or more halogen, OH, CN, NO_2 or C_{1-4} alkoxy or alkoxycarbonyl.

Exemplary preferred species according to the structure defined in the preceding paragraph include those wherein R_7 is phenyl substituted in the ortho positions independently with halogen, CF_3, NO_2, C_{1-3} alkyl, alkoxy or alkoxycarbonyl and substituted in the meta and para positions with halogen, CF_3 or C_{1-4} alkyl;

R_6 is H, C_{1-4} acyl or a single equivalent of a metal ion and

X and Y are independently H, phenyl, alkyl, alkenyl or alkynyl having up to 6 carbon atoms.

Preferred species according to the preceding description include the following:

N-(2,6-Dichlorophenyl)-6,7-dihydro-N,5,6-trimethyl-7-oxo[1,2,4]triazolo[1,5-a][1,3,5]-triazine-2-sulphonamide;

N-(2,6-Dichlorophenyl)-6,7-dihydro-5,6-dimethyl-7-oxo[1,2,4]triazole[1,5-a][1,3,5]-triazine-2-sulphonamide;

N-(2,6-dichlorophenyl)-6,7-dihydro-5,6-dimethyl-7-thioxo-[1,2,4]triazolo[1,5-a]-[1,3,5]-triazine-2-sulphonamide;

N-(2,6-Dichlorophenyl)-6,7-dihydro-5,6-dimethyl-7-thioxo-[1,2,4]triazolo[1,5-a][1,3,5]triazine-2-sulphonamide;

N-(2,6-Dichloro-3-methylphenyl)-6,7-dihydro-5,6-dimethyl-7-thioxo-[1,2,4]triazolo[1,5-a][1,3,5]-triazine-2-sulphonamide;

6,7-Dihydro-5,6-dimethyl-N-(2-methyl-6-nitrophenyl)-7-thioxo-[1,2,4]triazolo-[1,5-a]-[1,3,5]-triazine-2-sulphonamide;

N-(2-Chloro-6-fluorophenyl)-6,7-dihydro-5,6-dimethyl-7-thioxo-[1,2,4]triazolo[1,5-a][1,3,5]-triazine-2-sulph namide;

Preferr d species according to the preceding description include the following:

N-(2,6-Dichlorophenyl)-6,7-dihydro-5,6-dimethyl-3-methoxycarbonyl-7-oxopyrazolo[1,5-a][1,3,5]-triazine-2-sulphonamide;

N-(2,6-Difluorophenyl)-6,7-dihydro-5,6-dimethyl-3-methoxycarbonyl-7-thioxopyrazolo[1,5-a][1,3,5]-triazine-2-sulphonamide;

N-(2,6-Difluorophenyl)-6,7-dihydro-5,6-dimethyl-3-methoxycarbonyl-7-oxopyrazolo[1,5-a][1,3,5]-triazine-2-sulphonamide;

N-(2,6-Dichlorophenyl)-6,7-dihydro-5,6-dimethyl-3-methoxycarbonyl-7-thioxopyrazolo[1,5-a][1,3,5]-triazine-2-sulphonamide;

N-(2,6-Dichloro-3-methylphenyl)-6,7-dihydro-5,6-dimethyl-3-methoxycarbonyl-7-oxopyrazolo[1,5-a]-[1,3,5]-triazine-2-sulphonamide;

N-(2,6-Dichloro-3-methylphenyl)-6,7-dihydro-5,6-dimethyl-3-methoxycarbonyl-7-thioxopyrazolo-[1,5-a][1,3,5]-triazine-2-sulphonamide;

N-(2-Chloro-6-fluorophenyl)-6,7-dihydro-5,6-dimethyl-3-methoxycarbonyl-7-oxopyrazolo-[1,5-a][1,3,5]-triazine-2-sulphonamide;

N-(2-Chloro-6-fluorophenyl)-6,7-dihydro-5,6-dimethyl-3-methoxycarbonyl-7-thioxopyrazolo-[1,5-a][1,3,5]-triazine-2-sulphonamide;

N-(2-Chloro-6-methylphenyl)-6,7-dihydro-5,6-dimethyl-3-methoxycarbonyl-7-oxopyrazolo-[1,5-a][1,3,5]-triazine-2-sulphonamide;

N-(2-Chloro-6-methylphenyl)-6,7-dihydro-5,6-dimethyl-3-methoxycarbonyl-7-thioxopyrazolo-[1,5-a][1,3,5]-triazine-2-sulphonamide;

N-(2,6-Dibromophenyl)-6,7-dihydro-5,6-dimethyl-3-methoxycarbonyl-7-oxopyrazolo[1,5-a][1,3,5]-triazine-2-sulphonamide;

N-(2,6-Dibromophenyl)-6,7-dihydr -5,6-dimethyl-3-methoxycarbonyl-7-thioxopyrazolo[1,5-a][1,3,5]-triazin -2-sulf namide.

The preceding emb diments f triaz lo- and imidazolopyrimidine sulfonamide herbicides according to Formula I used in this invention are characterized by the R moiety $-SO_2N(R_6)(R_7)$. In the following embodiments analogous herbicides used herein are characterized by the R moiety $-N(R_4)SO_2-R_5$. In these embodiments both A and B are N, although it is within the purview of the invention to replace either A or B with the $=CR_3-$ moiety as with the foregoing embodiments.

The first group of compounds according to this embodiment of analogous compounds described in the preceding paragraph are those wherein R_1 and R_2 are combined to form the above bivalent radical (a), i.e.,

$$\text{(a)} \qquad -N = \overset{\overset{\displaystyle Z}{|}}{C} - \overset{\overset{\displaystyle Y}{|}}{C} = \overset{\overset{\displaystyle X}{|}}{C} -$$

or their tetrahydro analogs of bivalent radical (b) above, i.e.,

$$\text{(b)} \qquad - NH - \overset{\overset{\displaystyle Z}{|}}{CH} - \overset{\overset{\displaystyle Y}{|}}{CH} - \overset{\overset{\displaystyle X}{|}}{CH} -$$

wherein X, Y, Z, R_4 and R_5 of Formula I have the same meanings as those described earlier herein.

Preferred compounds within this embodiment of herbicidal compounds are those wherein

Y and R_4 are H;

X and Z are H or C_{1-4} alkyl or alkoxy and

R_5 is phenyl substituted in a first ortho position with halogen, NO_2, CF_3, CN, carboxyl or C_{1-4} alkoxycarbonyl; in the other ortho position in H, halogen or C_{1-4} alkoxycarbonyl and in the meta position adjacent said first ortho position with H, halogen or C_{1-4} alkyl.

Preferrred species in the foregoing group of compounds include the following:

N-5,7-dimethyl-4,5,6,7-tetrahydro-1,2,4-triazolo-[1,5-a]-pyrimidine-2-yl-2-(2,6-dichlorophenyl)-sulfonamide;

Exemplary compounds within this group include the following compounds wherein R_5 is a substituted phenyl radical:

N-(5,7-dimethyl)-6,7-dihydro-[1,2,4]-triazole-[1,5-a][1,3,5]-triazine-2-(2,6-difluorophenyl)-sulfonamide;

N-(5-methyl)-6,7-dihydro-[1,2,4]-triazole[1,5-a]-[1,3,5]-triazine-2-(2,6-difluorophenyl)-sulfonamide;

N-(7-methoxy0-6,7-dihydro-[1,2,4]-triazole[1,5-a]-[1,3,5]-triazine-2-(2,6-dichlorophenyl)-sulfonamide;

N-(5,7-dimethoxy)-6,7-dihydro-[1,2,4]-triazole-[1,5-a][1,3,5]-triazine-2-(2,3,6-trimethyl-phenyl)sulfonamide;

N-(5-chloro)-6,7-dihydro-[1,2,4]-triazole[1,5-a]-[1,3,5]-triazine-2-(2-acetyl-6-methylphenyl)-sulfonamide and

N-(5-methoxymethyl)-6,7-dihydro[1,2,4]-triazole-[1,5-a][1,3,5]-triazine-2-(2,6-difluorophenyl)-sulfonamide.

Other preferred compounds are those wherein R_5 is a substituted pyrazolyl, furanyl or thiophenyl radical. Representative R_5 pyrazolyl members are the pyrazol-4-yl sulfonamide compounds (un)substituted in the 1-position with C_{1-4} alkyl or phenyl and in the 3- and 5-positions with halogen, CN, NO_2, CF_3, phenyl, benzyl, C_{1-4} alkyl, aminocarbonyl, mono- or dialkylamino carbonyl, alkoxycarbonyl, alkenyloxycarbonyl or alkynyloxycarbonyl, benzyloxycarbonyl or said phenyl and benzyl members substituted with halogen, C_{1-4} alkyl or alkoxy.

Representative R_5 furanyl and thiophenyl members are the 2-yl and 3-yl isomers substituted in the substitutable positi ns of th 2-yl radical with one or more H, halog n or C_{1-4} alkyl and in th 3-yl radical with one or more H, halogen or COO-alkyl, -alkenyl or

carbonyl r alkoxyalkoxy; a 2-(C_{1-4} alk xycarb nyl) thiophen-3-yl radical; a pyridin-2-yl radical substituted in the 3-position with a C_{1-3} alkylsulfonyl or N,N-C_{1-3} dialkyl radical; pyrazol-3-yl, pyrazol-4-yl or pyrazol-5-yl radical or an imidazol-2-yl, imidazol-4-yl or imidazol-5-yl radical, said pyrazolyl- and imidazolyl-radicals being substituted in the 1 (or N)-position with H or a C_{1-8} alkyl, preferably C_{1-3} alkyl radical, and in the substitutable positions with H, halogen, preferably bromo or chloro, NO_2, C_{1-4} alkyl, alkoxy, mono- or dialkylamino, or dialkylaminosulfonyl, alkylsulfinyl, alkylsulfonyl, thioalkyl or alkoxycarbonyl radical and

R_{12} is a pyrimidin-2-yl or 1,3,5-triazin-2-yl radical independently substituted in the 4- and 6-positions, respectively, with C_{1-4} alkyl, preferably methyl, alkoxy, preferably methoxy, and/or difluoromethoxy radicals.

Preferred herbicidal sulfonylureas according to Formula II include:

Benzenesulfonamide, 2-chloro-N-[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl], (common name "chlorsulfuron");

Benzoic acid, 2-[[[[(4-chloro-6-methoxy-2-pyrimidin-2-yl)amino]carbonyl]amino]sulfonyl]-ethyl ester, (common name "chlorimuron ethyl");

2-Thiophenecarboxylic acid, 3-[[[[(4,6-dimethoxy-1,3,5-triazin-2-yl)amino]-carbonyl]amino]sulfonyl]-, methyl ester, (code number DPX-M6316);

Benzoic acid, 2-[[[[(4,6-dimethyl-2-pyrimidin-2-yl)amino]carbonyl]amino]sulfonyl]methyl ester, (common name "sulfometuron methyl");

N-[(4,6-dimethoxypyrimidin-2-yl)amin carbonyl]-4-ethoxycarbonyl-1-methylpyrazole-5-sulfonamide, (common name "pyrazolsulfuron ethyl"' code number "NC-311");

Methyl, [[[[N-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-methylamino]carbonyl]amino]-sulfonyl]benzoate, (common name "tribenuron methyl"; Code No. DPX-L5300);

Benzoic acid, 2-[[[[(4-methylamino-6-ethoxy-1,3,5-triazin-2-yl)amino]carbonyl]amino]-sulfonyl]-methylester, (common name "ethametsulfuron methyl"; Code No. DPX-7881);

3-(4,6-dimethoxy-2-pyrimidin-2-yl)-1-(N-methyl-N-methylsulfonylaminosulfonyl)urea, (common name "amidosulfuron");

N[(4,6-dimethylpyrimidin-2-yl)aminocarbonyl]-1-(1-methylethyl)-1H-imidazole-2-sulfonamide;

N-[(4-methoxy-6-methylpyrimidin-2-yl)aminocarbonyl]-1-(1-methylethyl)-1H-imidazole-2-sulfonamide;

N-[(4,6-dimethoxypyrimidin-2-yl)aminocarbonyl]-1-(1-methylethyl)-1H-imidazole-2-sulfonamide;

N-[(4,6-dimethylpyrimidin-2-yl)aminocarbonyl]-1-ethyl-1H-imidazole-2-sulfonamide;

N-[(4-methoxy-6-methylpyrimidin-2-yl)aminocarbonyl]-1-ethyl-1H-imidazole-2-sulfonamide;

N-[(4,6-dimethoxypyrimidin-2-yl)aminocarbonyl]-1-ethyl-1H-imidazole-2-sulfonamide;

3-pyridinecarboxylic acid, 2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-5-methyl-, ammonium salt;

2-(5-Methyl-5-trifluoromethyl-1-H-imidazol-4-on-2-yl)-pyridin-3-carboxylic acid;

2-(5-Methyl-5-trifluoromethyl-1-H-imidazol-4-on-2-yl)5-(m)ethyl isonicotinic acid;

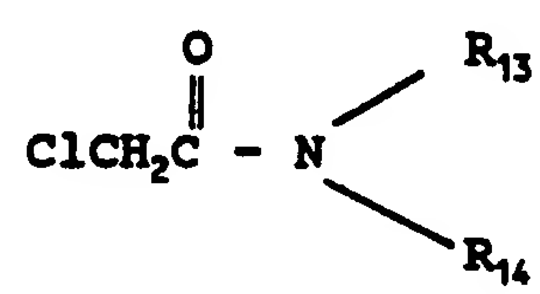
2-[5-(1-Fluoroethyl)-5-(m)ethyl-H-imidazol-4-on-2-yl]isonicotinic acid;

2-(5-(Difluoromethyl-5-(m)ethyl-1-H-imidazol-4-on-2-yl]-5-(m)ethyl-isonicotinic acid;

2-(5-(1-Fluoroethyl)-5-(m)ethyl)-imidazol-4-on-2-yl]isonicotinic (m)ethyl ester.

Another preferred class of compounds useful as the herbicidal component herein includes α-chloroacetamides according to Formula III

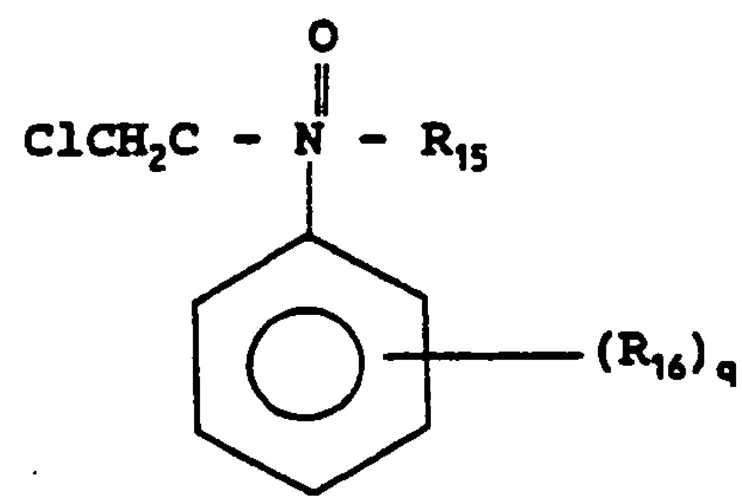
III



wherein R_{13} and R_{14} are independently hydrogen; C_{1-8} alkyl, alkoxy, alkoxyalkyl, acylaminomethyl, acyl-lower alkyl-substituted aminomethyl; cycloalkyl, cycloalkylmethyl, mono- or polyunsaturated alkenyl, alkynyl, cycloalkenyl, cycloalkenylmethyl having up to 8 carbon atoms; phenyl; or C_{4-10} heterocyclyl or heterocyclylmethyl containing from 1 to 4 ring hetero atoms selected independently from N, S or O; and wherein said R_{13} and R_{14} members may be substituted with alkyl, alkenyl, alkynyl, alkenyloxy, alkynyloxy, alkoxy, alkoxyalkyl, alkoxycarbomethyl or ethyl having up to 8 carbon atoms; nitro; halogen; cyano; amino or C_{1-4} alkyl-substituted amino; and wherein R_{13} and R_{14} may be combined together with the N atom to which attach d to form one of said heterocyclyl or substituted-heterocyclyl members.

An ther important subgenus f preferred α-haloacetamide compounds useful as the herbicidal component herein are the α-chloroacetanilides according to Formula IV

IV



wherein

R_{15} is hydrogen, C_{1-6} alkyl, haloalkyl, alkoxy or alkoxyalkyl, alkenyl, haloalkenyl, alkynyl or haloalkynyl having up to 6 carbon atoms, C_{5-10} heterocyclyl or heterocyclylmethyl having O, S and/or N atoms and which may be substituted with halogen, C_{1-4} alkyl, carbonylalkyl or carbonylalkoxyalkyl, nitro, amino or cyano groups;

R_{16} is hydrogen, halogen, nitro, amino, C_{1-6} alkyl, alkoxy or alkoxyalkyl, and

q is 0-5.

Examples of important acetamide herbicides according to Formulae III and IV are the following:

2-chloro-N-isopropylacetanilide (common name "propachlor");

2-chloro-1',6'-diethyl-N-(methoxymethyl)-acetanilide (common name "alachlor");

2-chloro-2',6'-diethyl-N-(butoxymethyl)-acetanilide (common name "butachlor");

2-chloro-N-(ethoxymethyl)-6'-ethyl-o-aceto-toluidide (common name "acetochlor");

Ethyl ester of N-chloroacetyl-N-(2,6-di-ethylphenyl)glycine (common name "di thatyl ethyl");

A larger group of preferred α-chl roacetamide and α-haloacetanilide herbicides includes the particular preferred species of Formulae III and Iv identified above.

Yet another class of preferred compounds useful as the herbicidal component in the composition/method according to this invention are the thiocarbamates.

Examples of important thiocarbamate herbicides are the following:

<u>cis-/trans</u>-2,3-dichloroallyl-diisopropylthiolcarbamate (common name "diallate");

Ethyl dipropylthiocarbamate (common name "EPTC");

S-ethyl diisobutyl (thiocarbamate) (common name "butylate");

S-propyl dipropyl(thiocarbamate) (common name "vernolate");

2,3,3-trichloroallyl-diisopropylthiocarbamate (common name "triallate").

A second component of the composition and method according to this invention is the biocidal compound. As used herein the terms "biocide(s)", "biocidal" or variations thereof refer to compounds and effects thereof used to eradicate non-plant, non-vegetal pests. Examples of such pests are insects, fungicides, nematodes, mites, etc. Contemplated herein are such non-vegetal pesticides as interact with the herbicidal component in the absence of the antidotal component to effect a negative synergism between the herbicide and biocide.

Particularly problematic biocides giving rise to negative synergism are various insecticides such as the organophosphates ("OPs"), carbamates, pyrethroids, cyclopropanecarb xylic acids and esters, carboxamides, dicarboximides, perchlorocyclohexane, etc. Because of

The chemical names of the above insecticides, fungicides, nematicides and miticides are set forth, e.g., in the Farm Chemicals Handbook '88 and other sources of chemical compounds.

The third essential component of the composition/method according to this invention is the antidotal compound. This compound must be present in an amount sufficient to inhibit, nullify, reduce, mitigate or prevent negative synergism from the interaction of the herbicidal and biocidal components of the invention. This is an important and distinguishing feature of the invention herein vis-a-vis prior art and, indeed, current antidote technology and practice, wherein the objective was and is to utilize the minimum amount of antidote required to safen the known or exhibited normal, inherent herbicidal property (phytotoxicity) of a given herbicide or combination of herbicides. In contrast, the antidote technology of this invention has as its purpose the safening of enhanced herbicidal activity beyond that normally or inherently exhibited by a herbicide(s), i.e., negative synergy, generated by the interaction of a herbicide and a biocide, commonly an insecticide, especially an OP insecticide.

Thus, in prior and current practice, a herbicide product may normally cause a commercially-unacceptable amount of injury to a crop at a given application rate in the absence of an antidote. However, that crop injury at the same herbicide application rate may be readily prevented by using the necessary amount of an effective antidote.

Further, agrichemical practice has been and is to discover and use herbicidal products which can be safely used in crops without an antidote, and numerous such products have been introduced to the market. Still, a serious technical and economic problem involving many of these important unsafened herbicides is that upon contact of some herbicides with loci

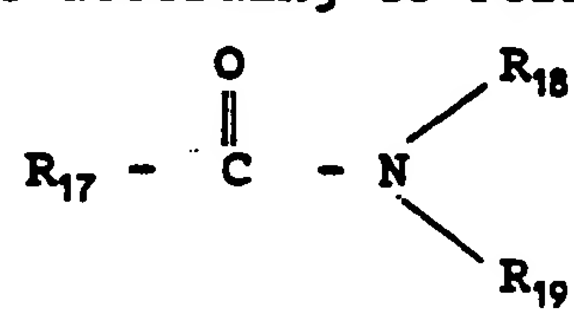
n rmally sufficient to safen the normal, inherent herbicidal property of a compound) to prevent or mitigate the negative synergy.

The requisite amount of antidote is determinable by routine experimentation well within the skill of the art. There is no critical range of concentrations of herbicide:biocide:antidote, as the ratios of these components will vary considerably over wide ranges depending upon a plurality of factors, such as the particular herbicide, biocide and antidote system involved. The biological properties of each of these components is known to vary considerably, both inherently and under the specific edaphic and climatic conditions of use, e.g., soil, moisture, light, as well as susceptibility to injury of crop and weed species by the herbicide and other parameters. The critical feature of the invention is that whatever the properties of the herbicide/biocide/antidote system involved, inherent and/or environmental-use related, the amount of antidote employed will be such as to negate in part or full the negative synergy induced by the particular herbicide/biocide interaction.

It is understood and appreciated that various combinations of said components, amounts thereof and application modes, e.g., in tank-mix form, PPI, preemergence, in-furrow, post-emergence, etc. will have varying degrees of efficacy in reducing negative synergism, hence some experimentation may be necessary in order to reach optimum results, but this will be within the skill of the art.

The antidotal compounds encompassed herein are:

(a) those according to Formula V

V 

alkoxycarbonyl; haloalkoxycarbonyl; halophenylcarbamyloxyalkyl; cycloalkenyl; phenyl; substituted phenyl wherein said substituents can be selected from alkyl, halogen, haloalkyl, alkoxy, haloalkylamido, phthalamido, hydroxy, alkylcarbamyloxy, alkenylcarbamyloxy, alkylamido, haloalkylamido or alkylcarboalkenyl; phenylsulfonyl; substituted phenylalkyl wherein said substituents can be selected from halogen or alkyl; dioxyalkylene, halophenoxyalkylamidoalkyl; alkylthiodiazolyl; piperidyl; piperidylalkyl; dioxolanylalkyl, thiazolyl; alkylthiazolyl; benzothiazolyl; halobenzothiazolyl; furyl; alkyl-substituted furyl; furylalkyl; pyridyl; alkylpyridyl; alkyloxazolyl; tetrahydrofurylalkyl; 3-cyano, thienyl; alkyl-substituted thienyl; 4,5-polyalkylene-thienyl; α-haloalkylacetamidophenylalkyl; α-haloalkylacetamidonitrophenylalkyl; α-haloalkylacetamidohalophenylalkyl; cyanoalkenyl;

R_{18} and R_{19} when taken together can form a structure consisting of piperidinyl; alkylpiperidinyl; pyridyl; di- or tetrahydropyridinyl; alkyltetrahydropyridyl; morpholyl; alkylmorpholyl; azabicyclononyl; diazacycloalkanyl; benzoalkylpyrrolidinyl; oxazolidinyl; perhydrooxazolidinyl; alkyloxazolidyl; furyloxazolidinyl; thienyloxazolidinyl; pyridyloxazolidinyl; pyrimidinyloxazolidinyl; benzooxazolidinyl; C_{3-7} spirocycloalkyloxazolidinyl; alkylaminoalkenyl; alkylideneimino; pyrrolidinyl; piperidonyl; perhydroazepinyl; perhydroazocinyl; pyrazolyl; dihydropyrazolyl; piperazinyl; perhydro-1,4-diazepinyl; quinolinyl; isoquinolinyl; dihydro-, tetrahydro- and perhydroquinolyl- or -isoquinolyl; indolyl and di- and perhydroindolyl and said combined R_{17} and R_{18} members substituted with those independent R_{17} and R_{18} radicals enumerated above;

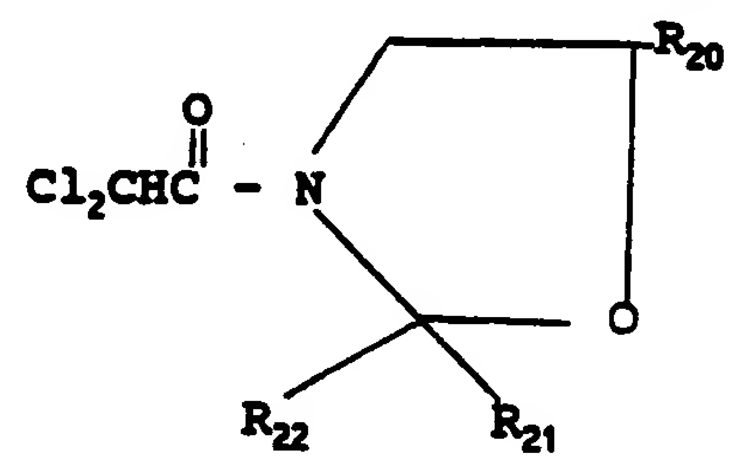
(b) one of the following compounds

α-[(Cyanomethoxy)imino]benzeneacetonitrile (common name "cyometrinil"),

One group f pref rred antidotal compounds includes those according to Formula V wherein R_{17} is C_{1-3} haloalkyl, R_{18} and R_{19} are independently C_{2-4} alkenyl or haloalkenyl or 2,3-dioxolan-2-yl-methyl and R_{18} and R_{19} when combined form a C_{4-10} saturated or unsaturated heterocyclic ring containing O, S and/or N atoms and which may be substituted with C_{1-5} alkyl, haloalkyl, alkoxy, or alkoxyalkyl or haloacyl groups. The preferred haloalkyl R_{17} member in Formula V is dichloromethyl. Preferred species in this group of antidotal compounds are N,N-diallyl-dichloroacetamide and N-(2-propenyl)-N-(1,3-dioxolanylmethyl)dichloroacetamide (Code No. PPG-1292).

Still more preferred antidotal compounds according to Formula V is a sub-group of substituted 1,3-oxazolidinyl dichloroacetamide having the formula

VI



wherein R_{20} is hydrogen, C_{1-4} alkyl, alkylol, haloalkyl or alkoxy, C_{2-6} alkoxyalkyl, a bicyclic hydrocarbon radical having up to 10 carbon atoms, phenyl or a saturated or unsaturated heterocyclyl (or heterocyclylmethyl) radicals having C_{4-10} ring atoms and containing O, S and/or N atoms, or said phenyl, heterocyclyl, and heterocyclylmethyl radicals substituted with one or more C_{1-4} alkyl, haloalkyl, alkoxy, alkoxyalkyl, halogen or nitro radicals, and

R_{21} and R_{22} are independently hydrogen, C_{1-4} alkyl or hal alkyl, phenyl or a heterocyclyl

1,5-Diazacyclononane, 1,5-bis-(dichloro-acetyl,

1-Azaspiro[4,4]nonane, 1-(dichloroacetyl),

Pyrrolo[1,2-a]-pyrimidine-[6(2H)]-one, 1-(dichloroacetyl)hexahydro-3,3,8a-trimethyl,

2,2-Dimethyl-3-(dichloroacetyl)-1,3-oxazole

2,2-Dimethyl-5-methoxy-3-(dichloroacetyl)-1,3-oxazole and

(N-(2-propenyl)-N-(1,3-dioxolan-2-ylmethyl)-dichloroacetamide (Code number PPG-1292).

Still another preferred group of antidotal compounds are the following which have a structure not according to Formula V, i.e., those in Paragraph (b) above:

α-[(Cyanomethoxy)imino]benzeneacetonitrile,

α-[(1,3-Dioxolan-2-yl-methoxy)imino]benzene-acetonitrile,

O-[1,3-Dioxolan-2-ylmethyl]-2,2,2-trifluoro-methyl-4'-chloroacetophenone oxime,

Benzenemethamine, N-[4-(dichloromethylene)-1,3-dithiolan-2-ylidene]-α-methyl, hydrochloride,

Diphenylmethoxy acetic acid, methyl ester,

1,8-Naphthalic anhydride,

4,6-Dichloro-2-phenyl-pyrimidine,

2-Chloro-N-[1-(2,4,6-trimethylphenyl)-ethenyl]acetamide,

Ethylene glycol acetal of 1,1-dichloro-acetone,

1,3-Dioxolane, 2-(dichloromethyl)-2-methyl-,

5-Thiazolecarboxylic Acid, 2-chloro-4-(trifluoromethyl)-, (phenylmethyl)-ester,

co-herbicides with the preferred ALS inhibit r classes of herbicides, i.e., sulfonylureas, imidazolinones and azolopyrimidine sulfonamides, are further exemplified below.

It is emphasized that the compositions of this invention are not limited to those the herbicidal component of which operates via the ALS inhibition or similar mode of action in a weed plant. More broadly this invention contemplates the inhibition or reduction of negative synergy arising from any combination of herbicidal and biocidal components, regardless of the mode of action in the plant's system, by means of a sufficient quantity of antidotal compound to effect weed control and crop safety.

As disclosed in more detail below, above compositions may be formed in a variety of ways, including tank mixing the said separate components for either bulk dispersal or for pre-packaging for storage, transportation, sale and use. Said compositions are also formed when the individual components are separately applied to the locus of use and there combine in contact with each other simultaneously or sequentially in any order. For example, the biocidal components may be first applied to the soil alone or together with the antidotal component, followed by application of the herbicidal component or the antidotal component may be applied to the seeds of the crop plant prior to planting in soil previously or subsequently treated with the biocidal component. The only caveat in forming said composition is that the antidotal component always be present to combat negative synergy.

The term "haloalkyl" embraces radicals wherein any one or more of the carbon atoms, preferably from 1 to 4 in number, is substituted with one or more halo groups, preferably selected from bromo, chloro and

By "antid tally- ffective" is meant the amount of antidote required to reduce the phytotoxicity level or effect of a herbicide, preferably by at least 10% or 15%, but naturally the greater the reduction in herbicidal injury the better.

By "herbicidally-effective" is meant the amount of the herbicide component (individual or plural) required to effect a meaningful injury or destruction to a significant portion of affected undesirable plants or weeds. Although of no hard and fast rule, it is desirable from a commercial viewpoint that 80-85% or more of the weeds be destroyed, although commercially significant suppression of weed growth can occur at much lower levels, particularly with some very noxious, herbicide-resistant plants.

The terms "antidote", "safening agent", "safener", "antagonistic agent", "interferant", "crop protectant" and "crop protective", are often-used terms denoting a compound capable of reducing the phytotoxicity of a herbicide to a crop plant or crop seed. The terms "crop protectant" and "crop protective" are sometimes used to denote a composition containing as the active ingredients, a herbicide-antidote combination which provides protection from competitive weed growth by reducing herbicidal injury to a valuable crop plant while at the same time controlling or suppressing weed growth occurring in the presence of the crop plant. Antidotes protect crop plants by interfering with the herbicidal action of a herbicide on the crop plants so as to render the herbicide selective to weed plants emerging or growing in the presence of crop plants.

Herbicides which may be used as co-herbicides with the azolopyrimidine sulfonamides of Formula I, the sulfonylureas of Formula II, α-haloacetamides of Formulae III or IV, the imidazolinones and thiocarbamate components of th invention composition and m thod with benefit in combination with an antidotes

Examples f important heter cyclyl phenyl ethers include:

5-(trifluoromethyl)-4-chloro-3-(3'-[1-ethoxycarbonyl]-ethoxy-4'-nitrophenoxy)-1-methylpyrazole;

5-(trifluoromethyl)-4-chloro-3-(3'-methoxy-4'-nitrophenoxy)-1-methylpyrazole;

5-(trifluoromethyl)-4-chloro-3-(3'-[1-butoxycarbonyl]-ethoxy-4'-nitrophenoxy)-4-methylpyrazole;

5-(trifluoromethyl)-4-chloro-3-(3'-methylsulfamoylcarbonyl propoxy-4'-nitrophenoxy)-4-methylpyrazole;

5-(trifluoromethyl)-4-chloro-3-(3'-propoxy-carbonylmethyloxime-4'-nitrophenoxy)-1-methylpyrazole;

(±)-2-[4-[[5-(trifluoromethyl)-2-pyridinyl]-oxy]phenoxy]propanoic acid.

Examples of important benzoic acid derivative herbicides include:

3,6-Dichloro-2-methoxybenzoic acid (common name "dicamba"),

2,5-Dichloro-3-aminobenzoic acid (common name "amiben" and "chloramiben"),

5-(2'-Chloro-4'-trifluoromethylphenoxy)-2-nitrobenzoic acid (common name "acifluorfen"),

2,6-Dichlorobenzonitrile (common name "dichlobenil"),

3,5,6-Trichloro-2-methoxybenzoic acid (common name "Tricamba"),

2,3,6-Trichlorobenzoic acid, and

2,3,5,6-Tetrachlorobenzoic acid,

and salts, esters and amides of the above acids.

herbicides, particularly th se of current commercial interest and use and those which may be determined of commercial utility.

Co-herbicidal compounds of preference include the following:

alachlor,
acetochlor,
butachlor,
metolachlor,
pretilachlor
metazachlor,
2-chloro-2',6'-dimethyl-N-(2-methoxyethyl)-acetanilide,
butylate and combinations thereof with the commercial antidotes R-29148 or PPG-1292 and EPTC and combinations thereof with the commercial antidotes R-25788, R-29148 or PPG-1292 any of which may further contain an extender, e.g., dietholate.

All of the above specifically-named antidotes and herbicides are known in the art.

As further detailed infra, while not necessary, the composition containing the herbicide/-biocide/antidote combination may also contain other additaments, e.g., fertilizers, inert formulation aids, e.g., surfactants, emulsifiers, defoamers, dyes, extenders, etc.

It will be recognized by those skilled in the art that all herbicides have varying degrees of phytotoxicity to various plants because of the sensitivity of the plant to the herbicide. Thus, e.g., although certain crops such as corn and soybeans have a high level of tolerance (i.e., low sensitivity) to the phytotoxic effect of alachlor, other crops, e.g., milo (grain sorghum), rice and wheat, have a low level of tolerance (i.e., high sensitivity) to the phytotoxic ffects of alachlor. The same type of sensitivity to herbicides as shown by cr p plants is also exhibit d by

a plant locus may be treated with a "tank-mix" composition containing a mixture of the herbicide, insecticide and the antidote which is "in combination". Or, the soil may be treated with the herbicide, insecticide and antidote compounds separately so that the "combination" is made on, or in, the soil. After such treat-treatments of the soil with a mixture of herbicide, insecticide and antidote or by separate or sequential application of the herbicide, insecticide and antidote to the soil, the herbicide, insecticide and antidote may be mixed into or incorporated into the soil either by mechanical mixing of the soil with implements or by "watering in" by rainfall or irrigation. The soil of a plant locus may also be treated with antidote by application of the antidote in a dispersible-concentrate form such as a granule. The granule may be applied to a furrow which is prepared for receipt of the crop seed and the herbicide and insecticide may be applied to the plant locus either before or after in-furrow placement of the antidote-containing granule so that the herbicide, insecticide and antidote form a "combination". Crop seed may be treated or coated with the antidote compound either while the crop seed is in-furrow just after seeding or, more commonly, the crop seed may be treated or coated with antidote prior to seeding into a furrow. The herbicide and insecticide may be applied to the soil plant locus before or after seeding and a "combination" is made when both herbicide, insecticide and antidote-coated seed are in the soil. Also contemplated as a "combination" is a commercially-convenient association or presentation of herbicide, insecticide and antidote. For example, the herbicide, insecticide and antidote components in concentrated form may be contained in separate containers, but such containers may be presented for sale or sold together as a "combination" (compositi n). Or, th h rbicide, insecticide and antidote components in concentrated form

applied to th surface of, or inc rporated in, the soil in which the seed has been planted. Or, the herbicide/-insecticide/antidote mixture may be applied to the soil, and then the seed thereafter "drilled" into the soil below the soil layer containing the herbicide/insecticide/antidote mixture. The herbicide will reduce or eliminate the presence of undesirable weed plants. Where the herbicide would by itself injure the crop seedlings, the presence of the antidote will reduce or eliminate the injury to the crop seed caused by the herbicide often exacerbated by an insecticide. It is not essential that the application of herbicide, insecticide and the antidote to the plant locus be made using the selected herbicide, insecticide and antidote in the form of a mixture or composition. The herbicide and the antidote or the insecticide and antidote may be applied to the plant locus in a sequential manner. For example, the insecticide and/or antidote may be first applied to the plant locus and thereafter the herbicide is applied. Or, the herbicide may be first applied to the plant locus and thereafter the antidote with or preceding application of the insecticide is applied.

The ratio of herbicide to antidote may vary depending upon the crop to be protected, weed to be inhibited, herbicide used, etc., but normally a herbicide-to-antidote ratio ranging from 1:25-to-60:1 (preferably 1:5-to-30:1) parts by weight may be employed, although much higher rates of antidote may be used, e.g., 1:100-1:300 parts by weight of herbicide-to-antidote. As indicated above, the antidote may be applied to the plant locus in a mixture, i.e., a mixture of a herbicidally-effective amount of herbicide and a safening-effective amount of an antidote, or sequentially, i.e., the plant locus may be treated with an effective amount of the herbicide followed by a treatment with the antidote or vice versa. In g neral, ffective herbicidal amounts are in the range of about 0.03 to about 12

carried or tractor-mounted spreaders, power dusters, boom and hand sprayers, spray dusters, and granular applicators. If desired, application of the compositions of the invention to plants can be accomplished by incorporating the compositions in the soil or other media.

The sequence of addition of chemicals is optional, but in common applications, the insecticide may be applied to the soil followed by application of the antidote alone or in admixture with the herbicide. Various sequential modifications of application of the chemicals is contemplated. In general, the herbicide, biocide and/or antidote may be applied preemergence by preplant incorporation surface application or postemergence. The only condition being that the insecticide and herbicide not be active in the plant in the absence of the antidote in order to prevent or reduce negative synergism induced by interaction of the herbicide and insecticide.

Evaluations of safening activity of representative antidote compounds of this invention were carried out using the specific procedures described below in greenhouse and field testing. Measurements of biological response as reported in the tables were made by visual observation and the degree of plant injury recorded in terms of percent injury.

Listed below are the names of various insecticidal compounds tested herein and representative ones for which data are reported in the tables.

Biocide No.	Nomenclature
1	S-[[(1,1-dimethyl-ethyl)thio]-methyl]O,O-diethylphosphorodithioate; (common name "terbufos", active ingredient in COUNTER®)

Listed below ar exemplary herbicidal and co-herbicidal compounds tested herein.

Herbicide No.	Nomenclature
1	N-[(4,6-dimethoxypyrimidin-2-yl)amino-carbonyl]-3-chloro-4-methoxycarbonyl-5-sulfonamide; (Code No. NC-319);
2	2-Chloro-2'-ethyl-6'-methyl-N-(ethoxy-methyl)acetanilide (common name "acetochlor")
3	2-Chloro-2',6'-diethyl-N-(methoxy-methyl)acetanilide (common name "alachlor");
4	2-Thiophenecarboxylic acid, 3-[[[[(4,6-dimethoxy-1,3,5-triazin-2-yl)amino]-carbonyl]amino]sulfonyl]-, methyl ester, (Code No. DPX-M6316);
5	Benzoic acid, 2-[[[[(4-chloro-6-methoxy-2-pyrimidin-2-yl)amino]-carbonyl]amino]sulfonyl]ethyl ester, (common name "chlorimuron ethyl");
6	3-Pyridinecarboxylic acid, 2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]5-ethyl (common name "imazathapyr")
7	Pyridine-3-[[[[(4,6-dimethyl-2-pyrimidin-2-yl)amino]carbonyl]amino]-sulfonyl] N,N-dimethylcarbamoyl (common name "nicosulfuron");

Herbicide N .	Nomenclature
15	Methyl, [[[[N-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-methylamino]carbonyl]amino]sulfonyl]benzoate (common name "tribenuron methyl", Code No. DPX-L5300);
16	3-Quinolinecarboxylic acid, 2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]- (common name "imazaquin");
17	3-Pyridinecarboxylic acid, 2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-5-methyl-, ammonium salt (Code No. AC 263,222);
18	3-Pyridinecarboxylic acid, 2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]- (common name "imazapyr");
19	Benzoic acid, 2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-4(or 5)-methyl- (Code No. AC 222,293);
20	5,5-Dimethyl-N-(2,6-dichloro-3-methylphenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide;
21	5-Methyl-N-(2,6-difluorophenyl)-1,2,4-triazolo[1,5-a]pyrimidine-2-sulfonamide (Code No. XRD-498);
22	5,7-Dimethyl-N-(2-nitrophenyl)-1,2,4-triaz lo[1,5-a]pyrimidin -2-sulfonamide;

with another antidote, R-29148, and a soil-life extender, dietholate, (ERADICANE® EXTRA). For purposes of this invention, when ERADICANE is used as the herbicide/antidote composition, it is to be provided that the biocidal component is an organophosphorus compound other than fonofos.

Co-Herbicide	Nomenclature
A	2-Chloro-N-(ethoxymethyl)-6'-ethyl-*o*-acetotoluidide ("acetochlor");
B	2-Chloro-1',6'-diethyl-N-(methoxy-methyl)acetanilide (common name "alachlor");
C	2-Chloro-N-(2-methoxy-1-methylethyl)-6'-ethyl-*o*-acetotoluidide ("metolachlor");
D	S-Ethyl dipropylcarbamothioate (common name "EPTC");
E	S-Ethyl-bis(2-methylpropyl)carbamo-thioate ("butylate");
F	Dimethylamine salt of 2-methoxy-3,6-dichlorobenzoic acid (common name "dimethylamine salt of dicamba");
G	2-[[4-Chloro-6-(ethylamino)-1,3,5-triazin-2-yl]amino]-2-methylpro-pionitrile (common name "calcium cyanamide" or "cyanazine");
H	2,4-Dichlorophenoxyacetic acid (common name "2,4-D");

Antidote No.	Nomenclature
7	5-Thiazolecarboxylic acid, 2-chloro-4-(trifluoromethyl)-, (phenylmethyl) ester,
8	Oxazolidine, 3-(dichloroacetyl)-2,2,5-trimethyl-,
9	Benzeneacetonitrile, alpha-<(cyano-methoxy)imino>-,
10	Oxazolidine, 3-(dichloroacetyl)-2,2-di-methyl-5-phenyl)-,
11	5-Oxazolecarboxylic acid, 2-<(2,2-dimethylethyl)amino>-4-(trifluoro-methyl)-, ethyl ester,
12	Acetic acid, (diphenylmethoxy)-, methyl ester (Code No. MON-7400),
13	Quinoline, 1-(dichloroacetyl)-1,2,3,4-tetrahydro-2-methyl-,
14	Isoquinoline, 2-(dichloroacetyl)-1,2,3,4-tetrahydro-,
15	Benzeneacetonitrile, alpha-{<(1,3-dioxolan-2-yl)methoxy>imino}-, (available only as Concep II™ sorghum seed),
16	1-Oxa-4-azaspiro<4.5>decane, 4-(dichloroacetyl)-,
17	1,5-Diazacyclononane, 1,5-bis(dichloro-acetyl)-,

Antidote No.	Nomenclature
31	Pyrimidine, 4,6-dichloro-2-phenyl-,
32	4-Pentenenitrile, 2-methyl-2-[(4-methylphenyl)thio]-,
33	Acetonitrile, [(5-chloro-8-quinolinyl)oxy]-,
34	Oxazolidine, 3-(dichloroacetyl)-2,2-dimethyl-5-(phenylmethyl)-,
35	Oxazolidine, 3-(dichloroacetyl)-2,2-dimethyl-5-(1-methyl-1H-pyrrol-2-yl)-,
36	Oxazolidine, 3-(dichloroacetyl)-5-(2-furanyl)-2-phenyl-,
37	Pyridinium, 3-(3-dichloroacetyl-2,2-dimethyl-5-oxazolidinyl)-1-methyl-, salt with trifluoromethanesulfonic acid (1:1),
38	Oxazolidine, 5-(2-benzofuranyl)-3-(dichloroacetyl)-2,2-dimethyl-,
39	Isoquinoline, 2-(dichloroacetyl)-1-ethyl-1,2,3,4-tetrahydro-,
40	Isoquinoline, 2-(dichloroacetyl)-1,2,3,4-tetrahydro-1-phenyl-,
41	Isoquinoline, 2-(dichloroacetyl)-1,2,3,4-tetrahydro-1-(2-methylpropyl)-,

Antidote No.	Nomenclature
54	Acetic acid, (diphenylmethoxy)-, 2-propynyl ester,
55	Acetic acid, (diphenylmethoxy)-, 3-furanylmethyl ester,
56	Acetic acid, [bis(2,6-dimethylphenyl)-methoxy]-,
57	Acetic acid, (diphenylmethoxy)-, 3-nitrophenyl ester,
58	Acetic acid, {[bis(2,6-dimethyl-phenyl)]methoxy}-, ethyl ester,
59	Acetic acid, (diphenylmethoxy)-, 1-cyano-1-methylethyl ester,
60	5-Thiazolecarboxylic acid, 2-chloro-4-(trifluoromethyl)-, ethyl ester,
61	5-Thiazolecarboxylic acid, butyl ester, 2-chloro-, 4-(trifluoromethyl)-,
62	5-Thiazolecarboxylic acid, 2-chloro-, hexyl ester, 4-(trifluoromethyl)-,
63	5-Thiazolecarboxylic acid, 2-chloro-4-(trifluoromethyl)-, octyl ester,
64	5-Thiazolecarboxylic acid, 2-chloro-4-(trifluoromethyl)-, phenyl ester,
65	5-Thiazolecarboxylic acid, 2-chloro-4-(trifluoromethyl)-,

Antidote No.	Nomenclature
76	Ethanimidamide, N'-[(methoxycarbonyl)-oxo]-2-(8-quinolinyloxy)-,
77	1(3H)-Isobenzofuranone, 3-[2-(2,5-dimethoxyphenyl)-2-oxoethyl]-,
78	Acetic acid, 2-(diphenylmethoxy) sodium salt hemihydrate,
79	Acetic acid, 2-(diphenylmethoxy)- and
80	Acetic acid, (diphenylmethoxy)-, 2-propanamine salt.

Greenhouse tests with the above compounds were conducted according to general Procedures I-VIII described below, with modifications noted in the relevant examples.

Procedure I

The following procedure shows interaction between herbicide and antidote when both are incorporated in a soil cover layer before emergence of crop and weed species. Containers were filled and compacted with a fumigated silt loam top soil to a depth of about 1.3 cm from the top of the container. A first container was designated as an untreated control, a second container was designated as a herbicide control, and a third container was designated as a herbicide + antidote test container. Each of the containers was seeded with a crop species. A measured amount of herbicide dispersed or dissolved in acetone was applied to a measured quantity of soil. To this same quantity of soil treated with herbicide, there was added a measured amount of antidote dispersed or dissolved in acetone. The quantity of soil treated with the herbicide and antidote was thoroughly mixed to incorporate the herbicide and

Antidote application rate was 0.55 mg active compound per inch of furrow (0.22 mg/cm). This rate was comparable to a plot application rate of 0.28 kilogram per hectare (kg/ha), based on 76 cm (30") spaced-apart furrows. Then, each of the second and third containers was filled and leveled with a cover layer of soil having incorporated therein the selected herbicide at a pre-determined concentration. The first container was filled and leveled with soil containing no herbicide. Insecticides were applied in the manner described in the examples below. Pots were overhead irrigated with 0.6 cm (1/4"), then placed on a bench in a greenhouse and sub-irrigated as required for the duration of the test. Plant response was observed about three weeks after initial treatment, unless otherwise indicated.

Procedure IV

The following procedure describes interaction among herbicide, biocide and antidote when they are incorporated in a soil cover layer before emergence of crop and weed species. Containers were filled and compacted with a steam sterilized silt loam soil to a depth of about 1.3 cm from the top of the container. A first container was designated as an untreated control, a second container was designated as a herbicide control, a third container was designated as a biocide control, a fourth container as a herbicide + biocide control and a fifth container as a herbicide + biocide + antidote test container. Each of the containers was seeded with a crop species and weed species. A measured amount of herbicide dispersed or dissolved in acetone was applied to a measured quantity of soil. The quantity of soil treated with the herbicide was thoroughly mixed to incorporate the herbicide. A sample of this soil was taken and used to cover the seed bed of the second container. A measured amount of the biocide formulated as granules or an acetone slurry of granules was applied to the soil previously treated with herbicide and this soil was thoroughly mixed t inc rp rate

soil previously treated with the biocide and the s il was thoroughly mixed to incorporate the antidote. This sample of soil was used to cover the seed bed of the fifth container (herbicide + biocide + antidote). For each test series, the seed beds of the first container (untreated control) and second container (herbicide control) were likewise covered by soil layers not treated with biocide or antidote. The containers were then placed on a bench in a greenhouse and subirrigated as required for the duration of the test. The herbicide, dispersed in water containing 0.25% nonionic surfactant (e.g., X-77) was applied by a track sprayer at a rate of approximately 187 L/ha to the emerged plants of the second, third and fourth containers about five days after planting ("DAP" in tables below). All treatments were run in duplicate. Plant response was observed according to Procedure V. Variations in this procedure will be noted in the examples.

Procedure VI

This procedure describes interaction among herbicide, biocide and antidote when the herbicide is incorporated in a soil cover layer and the biocide and the antidote are applied in a soil furrow containing crop seed before emergence of the crop. The soil and seeding depth were described in Procedure IV. A first container was designated as an untreated control, a second container was designated as a herbicide control, a third container was designated as a herbicide + biocide control and a fourth container as a herbicide + biocide + antidote test container. The biocide and antidote were formulated as granules. The biocide was applied to the soil furrows of the third and fourth containers at an application rate of 1.1 mg of active compound per cm of row. The antidote was applied to the soil furrow of the fourth container at an application rate of 0.37 mg of active compound p r cm of row. A measured amount of the herbicide dispersed or dissolved

Procedure VIII

This procedure describes interaction among herbicide, biocide and antidote when the biocide is applied to a soil furrow containing crop seed before emergence of the crop and the herbicide and antidote are applied after emergence of the crop and weeds. The soil and seeding depth was described in Procedure IV. A first container was designated as an untreated control, a second container was designated as a herbicide control, a third container was designated as a biocide control, a fourth container as herbicide + biocide control and a fifth container as a herbicide + biocide + antidote container. The biocide was formulated as a granule. The biocide was applied to the soil furrows of the third, fourth and fifth containers at an application rate of 1.1 mg of active compound per cm of row. The seed beds of the first through fifth containers were covered by a soil layer of untreated soil. The containers were then placed on a bench in a greenhouse and subirrigated as required for the duration of the test. The antidote, formulated in acetone:water (1:1) containing 0.25% v/v nonionic surfactant (X-77) was applied to the emerged plants of container five by a track sprayer (187 L/ha). Likewise the emerged plants of the second and third containers were sprayed with acetone:water (1:1) containing 0.25% nonionic surfactant (X-77). Similarly, the herbicide dispersed in water containing 0.25% nonionic surfactant (X-77) was applied to emerged plants of the second, fourth and fifth containers. The antidote and herbicide were applied six days after planting. All treatments were run in duplicate. Plant response was observed according to Procedure IV.

In the following examples, the observations for the various tests were made at the indicated times; unless otherwis indicated, all postemergence ("POE") tr atments for crops, e.g., corn and weeds were made at

Example 1

This example was designed to investigate the degree of corn injury by Herbicide No. 1 in contact with Insecticide Nos. 1 and 2 with and without the presence of Antidote No. 1.

The procedures used here involved a combination of Procedures II and III. Granulated Insecticide No. 1 (terbufos) was suspended in water and pipetted in-furrow over corn seeds. Insecticide No. 2 (chlorpyrifos) was sprayed onto cover layers and incorporated therein. Technical grade herbicide and antidote also were pipetted onto the cover layers and incorporated. After spreading the cover layers over the seedbeds, the containers were placed on greenhouse benches to receive 0.6 cm overhead irrigation and subsequent subirrigation as needed. Plant response was evaluated seven (7) weeks after test initiation. Percent injury shown is the mean of three (3) replicates. Results are shown in Table 1. The weed velvetleaf (Abutilon theophrasti) used in this and subsequent tests is abbreviated as "VELE".

Table 1 (continued)

Treatment			Percent Injury	
Insecticide No. (Rate)	Antidote No. 1 (Kg/Ha)	Herbicide No. 1 (Kg/Ha)	Corn	VELE
2 (3.36 kg/ha)	-	0.14	60	78
"	-	0.56	90	92
"	-	2.24	95	92
"	0.14	0.14	75	83
"	0.56	0.56	70	92
"	2.24	2.24	92	95
"	0.14	-	0	78
"	0.56	-	0	33
"	2.24	-	0	0
"	-	-	0	0
1 (H_2O) (crystals scattered in-furrow)	-	-	0	0
"	2	-	13	0
"	2	2	78	95

Table 2

Insecticide No. (Rate)	Antidote No. 1 (Kg/Ha)	Herbicide No. (Kg/Ha) 1	2	9	% Injury Corn	VELE
-	-	0.14	-	-	4	89
-	-	0.56	-	-	58	93
-	0.14	0.14	-	-	0	86
-	0.42	0.14	-	-	8	93
-	0.56	0.56	-	-	3	90
-	1.68	0.56	-	-	5	95
1 (0.23 Kg/305m)	-	0.14	-	-	83	83
"	-	0.56	-	-	96	95
"	0.14	0.14	-	-	18	83
"	0.42	0.14	-	-	6	90
"	0.56	0.56	-	-	33	95
"	1.68	0.56	-	-	34	93
1 (0.11 kg/305m)	-	0.14	-	-	83	93
"	-	0.56	-	-	93	94
"	0.14	0.14	-	-	26	78
"	0.42	0.14	-	-	6	84
"	0.56	0.56	-	-	30	93
"	1.68	0.56	-	-	18	95

Table 2 (continued)

Ins cticide No. (Rate)	Antidote No.1(Kg/Ha)	Herbicide No. (Kg/Ha) 1	2	9	% Injury Corn	VELE
1 (0.23 Kg/305m)	-	0.14	4.48	-	90	95
"	0.22	0.14	4.48	-	20	98
2 (3.36 Kg/Ha)	-	-	4.48	-	76	35
"	0.22	-	4.48	-	19	11
"	-	0.14	4.48	-	83	88
"	0.22	0.14	4.48	-	29	83
1 (0.23 Kg/Ha)	-	-	-	2.24	3	88
2 (3.36 Kg/Ha)	-	-	-	2.24	0	30

Table 3

Insecticide No. (Rate)	Antidote No. 1(Kg/Ha)	Herbicide No. (Kg/Ha) 1	2	9	% Injury Corn
-	-	0.14	-	-	10
-	-	0.56	-	-	63
-	0.14	0.14	-	-	3
-	0.42	0.14	-	-	3
-	0.56	0.56	-	-	8
-	1.68	0.56	-	-	3
3 (227g)	-	0.14	-	-	45
"	-	0.56	-	-	93
"	0.14	0.14	-	-	0
"	0.42	0.14	-	-	20
"	1.68	0.56	-	-	8
4 (227g)	-	0.14	-	-	55
"	-	0.56	-	-	45
"	0.14	0.14	-	-	3
"	0.42	0.14	-	-	5
"	0.56	0.56	-	-	28
"	1.68	0.56	-	-	5

It will be n ted that both Insecticides N . 3 (tefluthrin, a pyrethroid compound) and No. 4 (carbofuran, a carbamate compound), increased corn injury by Herbicide No. 1. At the 0.14 kg/ha rate for Herbicide No. 1, the corn injury was increased from 10% to 45% by Insecticide No. 3 and to 55% by Insecticide No. 4. This negative synergism induced by the interaction of herbicide and insecticide was reduced by Antidote No. 1 at 1:1 ratio to less than 5% in all cases. Moreover, the interaction between Herbicide No. 2 and Insecticide No. 3 resulting in 83% corn injury was reduced to 25% with a 0.22 kg/ha of Antidote No. 1, while the interaction of Herbicide No. 2 with Insecticide No. 4 caused 95% injury. Antidote No. 1 reduced that injury to 45% using only a 0.22 kg/ha rate.

Example 4

This example illustrates the interaction between the Insecticide No. 2 (chlorpyrifos) and three sulfonylureas, Herbicide No. 4 (DPX-M6316), No. 5 (chlorimuron ethyl), No. 1 (NC-319) and an imidazolinone compound. Herbicide No. 6 (imazethapyr). Again, Antidote No. 1 was used to evaluate its effect on any negative synergy induced by interaction of herbicide and insecticide.

The procedure used in this test was Procedure No. 2 above. Formulations of herbicide, insecticide and antidote were applied via track sprayer sequentially onto cover layers, incorporated into the soil which was spread over seedbeds, then irrigated from above with 0.6 cm water. Observations were made three (3) weeks after treatment. Results are shown in Table 4.

Table 4 (continued)

Treatment (kg/Ha) Insecticide No. 2	Antidote No. 1	Herbicide No.		% Injury Corn	VELE
-	0.14	6	(0.14)	3	28
3.36	-	6	(0.07)	65	30
"	0.07	6	(0.07)	5	15
"	-	6	(0.14)	43	20
"	0.14	6	(0.14)	63	40
-	-	1	(0.07)	2	20
-	-	1	(0.14)	13	67
-	0.07	1	(0.07)	0	8
-	0.14	1	(0.14)	10	43
3.36	-	1	(0.07)	0	10
"	0.07	1	(0.07)	0	23
"	-	1	(0.14)	38	20
"	0.014	1	(0.14)	0	53
"	-	-	-	0	0

Table 5

Treatment (Kg/Ha)				% Injury	
Insecticide N . 2	Antidote No. 1	Herbicide No. 1	Application Mode	Corn	VELE
-	-	0.14	PPI	5	78
-	-	0.56	"	28	93
-	-	2.24	"	58	95
1.68	-	0.14	"	18	90
"	-	0.56	"	10	90
"	-	2.24	"	87	98
-	0.14	0.14	"	0	85
-	0.56	0.56	"	5	80
-	2.24	2.24	"	0	93
1.68	0.14	0.14	"	0	90
"	0.56	0.56	"		93
"	2.24	2.24	"	0	93
"	2.24	-	"	0	0
-	-	0.07	POE	0	30
-	-	0.28	"	15	30
-	-	1.12	"	7	20
1.68	-	0.07	"	10	23
"	-	0.28	"	10	42
"	-	-	"	35	60
1.68	-	-	-	0	0

The above data indicat that post emergenc applications of Insecticide No. 2 increased herbicide injury from both PPI and POE applications of Herbicide No. 1, but not as dramatically as when soil applied. Antidote No. 1 safened PPI herbicide treatments with or without Insecticide No. 2.

Example 6

The tests described in this example were to determine the response to Herbicide No. 1 plus insecticides (No. 1 and No. 2) in sensitive (PN3320) and tolerant (PP3377) genotypes of corn.

The procedures in this example were the same as those described in Examples 1-3. The insecticides were formulated in water and pipetted in-furrow over the seeds. Technical grade herbicide and antidote were sequentially pipetted onto cover layers, incorporated and spread over the insecticide-treated pot seedbeds. An overhead irrigation of 0.6 cm was applied immediately after chemical application and the pots subsequently subirrigated on greenhouse benches as needed. Observations of plant response in two replications were taken three (3) weeks after treatment. Results are shown in Table 6; values for corn injury are the mean of duplicate replications.

Table 6 (continued)

Insecticide No. (Rate)	Antidote No. 1 (Kg/Ha)	Herbicide No. 1 (Kg/Ha)	% Corn Injury PN 3377	PN 3320
2 "	0.42	0.14	13	10
"	0.56	0.56	10	68
"	1.68	0.56	28	43

at the 4-7 leaf stage. Plots were small plot with 3 replications in a randomized complete block design. In the PRE and PPI herbicide treatments, Antidote No. 1 was applied as a tankmix in both treatments. In the POE herbicide treatments, that antidote was applied as a tank mix with the herbicide at the EP and LP stages.

In summary, as a mean of results from nine disparate locations, in both PRE and PPI application tests, Insecticide No. 1 increased herbicidal injury to corn from combinations of Herbicide No. 1 with Herbicide Nos. 2, 3 and from combinations of Herbicide Nos. 2 and 9. Increased injury expressed itself in terms of malformed plants, stand reduction and growth reduction. At a 1:1 ratio, Herbicide No. 1:Antidote No. 1 and at a 30:1 ratio of Herbicide No. 2:Antidote No. 1, crop injury was reduced from non-commercially-acceptable to commercially-acceptable levels in both PRE and PPI applications. Higher antidote rates of 1:3 (herbicide:antidote) improved corn tolerance even further. Antidote No. 1 provided safening of all crop injury expressions.

In the POE tests, data representing the mean of data from five different locations indicated insignificant interaction between Herbicide No. 1 and Insecticide No. 1 following POE applications of the herbicide following soil applications of the insecticide prior to planting the corn seed. Significant increased growth reduction of corn treated with Insecticide No. 1 occurred following late POE applications of Herbicide No. 8 and early and late POE applications of Herbicide No. 7. In addition, late POE applications of combinations of Herbicide Nos. 1 and 8 resulted in significant interactions with the insecticide.

Antidote No. 1 applied as a tankmix in POE applications, effectively safened insecticide interactions with POE applications of Herbicide No. 7.

The ab ve field trials demonstrated significant negative synergy induced in repr sentative

The examples which f ll w will describe a variety of modes of application of various herbicide, biocide and antidotal compounds to plant loci. Examples 8-20 describe preplant incorporation of the antidote and biocide followed by postemergence application of the herbicide according to Procedure V.

Example 8

In this example a variety of antidotal compounds were evaluated for their efficacy against negative synergy induced by the interaction of primi-sulfuron (Herbicide No. 8), active ingredient in BEACON® herbicide, and terbufos (Biocide No. 1) as the Counter® 15G granule. The safeners and terbufos (in granular form) were applied preplant incorporated ("PPI"), (band) and the herbicide applied postemergence ("POE") in corn in the presence of the weeds shattercane, giant foxtail and velvetleaf according to the description in Procedure V. In this test, five (5) days after PPI application of terbufos and safener, observations of plant response were made to determine the effects of the terbufos and safener, after which the herbicide was applied and observations made eight (8) days later. Plant response is thus reported in Table 7 below for five (5) and thirteen (13) days after planting (DAP) the seeds.

In this test the herbicide was applied at the rate of 0.07 kg/ha of active ingredient and the terbufos was applied at the rate of 8.96 kg/ha active ingredient; the safener rate was either 4.48 kg/ha or 8.96 kg/ha of active ingredient as shown in Table 7.

Table 7 (continued)

Herb. N . 8 (Kg/Ha)	Biocide No. 1 (Kg/Ha)	Antidote No.	Rate (Kg/Ha)	% Inhibition 5 DAP Corn	SHCA	VELE	13 DAP Corn	SHCA	VELE
0.07	8.96	8	4.48	20	0	10	35	90	85
"	"	10	"	0	0	0	25	75	90
"	"	16	"	0	0	0	45	90	95
"	"	20	"	15	0	0	30	75	95
"	"	23	"	20	0	0	30	85	95
"	"	1	"	10	0	0	25	80	90

Table 8

Herb. No. 8 (Kg/Ha)	Biocide No. 9 (Kg/Ha)	Antidote No.	Rate (Kg/Ha)	% Inhibition 5 DAP Corn	5 DAP SHCA	5 DAP VELE	13 DAP Corn	13 DAP SHCA	13 DAP VELE
0.07	-	-	-	0	0	0	0	75	85
"	8.96	-	-	20	30	0	65	80	90
"	"	29	4.48	35	40	20	65	85	95
"	"	4	8.96	15	30	0	30	65	90
"	"	5	"	20	70	0	35	85	90
"	"	77	"	15	60	20	65	90	95
"	"	30	4.48	10	25	80	56	95	95
"	"	7	8.96	20	20	0	15	75	90
"	"	12	4.48	20	15	20	20	75	85
"	"	15	8.96	30	40	60	35	85	90
"	"	24	4.48	10	20	0	55	80	95
"	"	31	"	15	20	0	65	80	85
"	"	32	"	20	30	0	70	80	85
"	"	33	"	30	70	60	20	90	90
"	"	2	"	20	20	0	45	85	85
"	"	6	"	10	30	0	35	80	90
"	"	8	"	20	30	0	30	80	90
"	"	10	"	20	30	0	30	70	90

Example 10

In another duplication of the procedure described in Examples 8 and 9, the biocide chorpyrifos (Biocide No. 2; active ingredient in LORSBAN® 15G) was used. Test results are shown in Table 9. The only difference in those tests were the dates of application of the chemicals and the dates of making observations.

Table 9 (continued)

Herb. No. 8 (Kg/Ha)	Biocide No. 2 (Kg/Ha)	Antidote No.	Rate (Kg/Ha)	% Inhibition 5 DAP Corn	SHCA	VELE	13 DAP Corn	SHCA	VELE
0.07	8.96	16	4.48	0	0	0	30	85	90
"	"	20	"	0	0	0	25	80	85
"	"	23	"	0	0	0	5	80	85
"	"	1	"	0	10	0	15	80	80

Table 10

Herb. No. 8 (Kg/Ha)	Biocide No. 10 (Kg/Ha)	Antidote No.	Rate (Kg/Ha)	% Inhibition 5 DAP Corn	5 DAP SHCA	5 DAP VELE	13 DAP Corn	13 DAP SHCA	13 DAP VELE
0.14	8.96	-	-	0	0	0	0	90	95
"	8.96	-	-	0	30	0	30	90	95
"	"	29	4.48	0	10	0	25	95	95
"	"	4	8.96	0	0	0	20	90	95
"	"	5	"	0	0	0	15	85	95
"	"	77	"	0	0	0	35	90	95
"	"	30	4.48	0	20	90	25	95	95
"	"	7	8.96	0	0	0	10	85	90
"	"	12	4.48	0	0	0	0	85	90
"	"	15	8.96	20	20	50	15	90	95
"	"	24	4.48	0	0	0	20	85	95
"	"	31	"	0	0	0	25	80	95
"	"	32	"	0	20	0	35	90	95
"	"	33	"	0	20	30	5	90	95
"	"	2	"	0	0	0	20	90	95
"	"	6	"	0	0	0	10	85	95
"	"	8	"	0	0	0	15	80	90
"	"	10	"	0	0	0	15	80	95

Referring to the test data in Tables 8-10, most of the antidotes were active in reducing corn injury arising from the interaction of the biocide and the later-applied herbicide. The most active antidotes were Nos. 1, 12 and 33. Other more active antidotes were Nos. 6-8, 10, 20 and 23. In these tests Antidote Nos. 31, 32 and 77 were either inactive or weakly active. Fifteen of the antidotes provided significant activity (i.e., > 20%) at least 75% of the time. Control of the test weeds with primisulfuron with or without the biocides and antidotes was at expected levels.

Evaluations of plant response to the biocides and safeners before application of the herbicide did not show significant harmful effect on the corn. For example, COUNTER and DYFONATE caused slight early stunting and leaf malformation to corn. Some injury was noted with combinations including Antidote Nos. 15, 30 and 33.

In a set of experiments parallel to those described in Examples 8-11, the same Procedure V was conducted, but using different herbicidal components and dates of PPI planting of biocide and antidote, POE application of herbicide and observation as described in Examples 12-15 below.

Example 12

In this example Herbicide No. 7, viz. ACCENT®, was used; active ingredient is nicosulfuron. The biocide was No. 1 (COUNTER 15G). The herbicide was applied POE at the above-mentioned leaf-stage of growth of the plants five (5) days after planting the seed and observations were made eight (8) days later, i.e., thirteen (13) days after planting. Test results are shown in Table 11.

Table 11 (continued)

Herbicide No. 7 (Kg/Ha)	Biocide No. 1 (Kg/Ha)	Antidote No.	Rate (Kg/Ha)	% Inhibition		
				Corn	SHCA	VELE
0.28	8.96	16	4.48	40	70	65
"	"	20	"	30	75	70
"	"	23	"	35	65	65
"	"	1	"	20	75	70
-	"	-	-	5	25	0

Table 12

Herbicide No. 7 (Kg/Ha)	Biocide No. 9 (Kg/Ha)	Antidote No.	Rate (Kg/Ha)	% Inhibition Corn	SHCA	VELE
0.56	-	-	-	0	75	60
"	8.96	-	-	55	80	70
"	"	29	4.48	50	80	70
"	"	4	8.96	30	70	65
"	"	5	"	30	75	65
"	"	77	"	35	85	75
"	"	30	4.48	50	90	100
"	"	7	8.96	40	85	65
"	"	12	4.48	10	65	70
"	"	15	8.96	40	95	85
"	"	24	4.48	30	70	65
"	"	31	"	40	85	75
"	"	32	"	65	85	70
"	"	33	"	20	75	70
"	"	2	"	35	80	70
"	"	6	"	30	75	60
"	"	8	"	30	85	70
"	"	10	"	40	80	70

Example 14

The procedure in the preceding examples was repeated using, however, Biocide No. 2 (LORSBAN® 15G). Planting of seeds and application of chemicals were at a different time than in Example 13, but the intervals between planting, application of herbicide and observation times were the same. In this example the ACCENT application rate was again 0.02 kg/ha as in Example 12. Test data are reported in Table 13.

Table 13 (continued)

Herbicide No. 7 (Kg/Ha)	Biocide No. 2 (Kg/Ha)	Antidote No.	Rate (Kg/Ha)	% Inhibition		
				Corn	SHCA	VELE
0.28	8.96	16	4.48	30	90	65
"	"	20	"	10	90	65
"	"	23	"	15	85	70
"	"	1	"	5	90	70
-	"	-	-	0	25	0

Table 14

Herbicide No. 7 (Kg/Ha)	Biocide No. 2 (Kg/Ha)	Antidote No.	Rate (Kg/Ha)	% Inhibition Corn	SHCA	VELE
0.84	-	-	-	0	75	65
"	8.96	-	-	40	70	65
"	"	29	4.48	35	80	70
"	"	4	8.96	15	70	65
"	"	5	"	10	70	70
"	"	77	"	25	85	70
"	"	30	4.48	30	90	100
"	"	7	8.96	25	75	70
"	"	12	4.48	0	75	70
"	"	15	8.96	25	95	80
"	"	24	4.48	20	80	65
"	"	31	"	45	75	65
"	"	32	"	35	70	60
"	"	33	"	0	75	75
"	"	2	"	20	75	70
"	"	6	"	15	75	75
"	"	8	"	20	85	70
"	"	10	"	20	70	65

From the data in Tables 11-14, it is seen that substantial corn injury (40 to 60%) resulted from treatments with 8.96 kg/ha of biocides (OP insecticides) followed by POE applications of ACCENT herbicide, resulting in enhanced herbicidal activity. By itself, with no insecticide present ACCENT, at rates within the range of 0.28 to 0.84 kg/ha was completely safe to corn.

Significant reduction in corn injury was seen with many of the test safeners. The most active safeners in these tests were Antidote Nos. 1, 12 and 33. Antidote Nos. 11 and 7, both milo seed protectants, had similar activity.

In most cases, control of the weeds shattercane and velvetleaf with safened combinations was at expected or slightly elevated levels.

In another set of experiments, using Procedure V, another herbicide, i.e., PURSUIT® (No. 18) was used to evaluate any interaction resulting from contact thereof with the same biocides used in Examples 8-15 and the safening effect of the same antidotes used in those examples. These experiments are described in Examples 16-19 below. In those experiments, the only changes in Examples 18 and 19 were different dates for planting, herbicide application and observation of plant response.

Example 16

In this test, the insecticide COUNTER® 15G was, together with the test antidotes planted by PPI, then five (5) days later, the herbicide, PURSUIT® 15G (active ingredient imazapyr), was applied POE and ten (10) days thereafter, plant response was observed and recorded. Because of its inherent high unit activity, the rate of application of PURSUIT was reduced to 0.0175 kg/ha. Test data are reported in Table 15.

Table 15 (continued)

Herbicide N . 18 (Kg/Ha)	Biocide No. 1 (Kg/Ha)	Antidote No.	Rate (Kg/Ha)	% Inhibition Corn	SHCA	VELE
0.0175	8.96	16	4.48	65	65	90
"	"	20	"	60	60	85
"	"	23	"	65	65	85
"	"	1	"	55	55	80
-	"	-	-	0	20	15

Table 16

Herbicide No. 18 (Kg/Ha)	Biocide No. 9 (Kg/Ha)	Antidote No.	Rate (Kg/Ha)	% Inhibition		
				Corn	SHCA	VELE
0.0175	-	-	-	5	40	65
"	8.96	-	-	45	60	70
"	"	29	4.48	35	75	75
"	"	4	8.96	35	55	70
"	"	5	"	25	40	65
"	"	77	"	15	55	70
"	"	30	4.48	35	60	100
"	"	7	8.96	30	50	75
"	"	12	4.48	20	55	65
"	"	15	8.96	15	50	75
"	"	24	4.48	30	55	65
"	"	31	"	45	50	70
"	"	32	"	55	55	70
"	"	33	"	10	60	80
"	"	2	"	25	45	70
"	"	6	"	25	50	70
"	"	8	"	30	45	75
"	"	10	"	20	60	70

Example 18

The procedure in the preceding example was followed except the insecticide was LORSBAN® 15G (Antidote No. 2), and, as noted above, the dates for planting, herbicide application and plant observation were different in this example; observation was nine (9) days after herbicide application. Results are show in Table 17.

Table 17 (continued)

Herbicide No. 18 (Kg/Ha)	Biocide No. 2 (Kg/Ha)	Antidote No.	Rate (Kg/Ha)	% Inhibition		
				Corn	SHCA	VELE
0.0175	8.96	16	4.48	60	65	85
"	"	20	"	55	60	80
"	"	23	"	50	65	85
"	"	1	"	45	60	80
-	"	-	-	0	30	0

Table 18

Herbicide No. 18 (Kg/Ha)	Biocide No. 10 (Kg/Ha)	Antidote No.	Rate (Kg/Ha)	% Inhibition		
				Corn	SHCA	VELE
0.0175	-	-	-	10	45	85
"	8.96	-	-	55	40	80
"	"	29	4.48	45	45	80
"	"	4	8.96	40	45	85
"	"	5	"	10	40	75
"	"	77	"	15	45	85
"	"	30	4.48	40	70	100
"	"	7	8.96	40	50	85
"	"	12	4.48	25	50	85
"	"	15	8.96	15	65	85
"	"	24	4.48	35	55	80
"	"	31	"	55	45	80
"	"	32	"	45	40	80
"	"	33	"	0	35	85
"	"	2	"	30	30	85
"	"	6	"	35	50	80
"	"	8	"	30	35	80
"	"	10	"	20	45	85

From the above series of tests to evaluate the safening effect of various antidotes on the negative synergy induced by the interaction of commercial insecticide applied PPI, followed by POE application of PURSUIT® herbicide, it is noted that severe corn injury did, in fact, result from said negative synergy. On the order of magnitude from 10% to 75% corn injury following interaction between PURSUIT and COUNTER.

Lesser, but increased corn injury (45% up to 65%) also resulted from the interaction of PURSUIT with DYFONATE, LORSBAN and THIMET.

The most active safeners in these tests were Nos. 11, 15 and 33. Of note, Antidote No. 11, was substantially more effective than No. 11 (flurazole, a commercial seed protectant for milo against acetanilide herbicide injury).

Control of the weeds was generally at expected levels for safened combinations of antidotes with PURSUIT.

In the preceding sets of tests, the herbicide application mode was postemergence according to Procedure V. Other sets of tests were conducted using the PPI method of herbicide application according to Procedure IV described above. In these tests, described in Examples 20-27 below, Herbicide Nos. 1 (NC-319; also, MON-12000) and 21 (XRD-498) were similarly contacted with COUNTER, DYFONATE, LORSBAN and THIMET insecticides and the same group of antidotes used in Examples 8-19. The only procedural difference in these examples is the dates on which the tests were initiated and plant response observations were made; intervals between those events were the same (11 or 12 days). In all of these tests the herbicide application rate was 0.14 kg/ha; the biocide rate was 8.96 kg/ha and the antidote rate was 4.48 kg/ha or 8.96 kg/ha.

Table 19

Herbicide No. 1 (Kg/Ha)	Biocide No. 1 (Kg/Ha)	Antidote No.	Rate (Kg/Ha)	% Inhibition		
				Corn	GIFT	VELE
0.0175	-	-	-	5	15	85
"	8.96	-	-	50	60	95
"	"	29	4.48	40	55	90
"	"	4	8.96	30	50	90
"	"	5	"	15	30	85
"	"	77	"	50	60	95
"	"	30	4.48	30	65	90
"	"	7	8.96	15	55	80
"	"	12	4.48	5	45	90
"	"	15	8.96	20	50	85
"	"	24	4.48	25	45	90
"	"	31	"	35	55	85
"	"	32	"	15	30	75
"	"	33	"	20	40	85
"	"	2	"	30	50	90
"	"	6	"	10	50	95
"	"	8	"	20	45	90
"	"	10	"	5	40	85

Example 21

The test reported in this example was a duplicate of that in the preceding example, but for substitution of DYFONATE 10G as the biocidal component. The test data for this example is shown in Table 20.

Table 20 (continued)

Herbicide No. 1 (Kg/Ha)	Biocide No. 9 (Kg/Ha)	Antidote No.	Rate (Kg/Ha)	% Inhibition		
				Corn	GIFT	VELE
0.0175	8.96	16	4.48	15	60	90
"	"	20	"	25	60	90
"	"	23	"	20	60	95
"	"	1	"	25	60	90
-	"	-	-	5	35	25

Table 21

Herbicide No. 1 (Kg/Ha)	Biocide No. 2 (Kg/Ha)	Antidote No.	Rate (Kg/Ha)	% Inhibition		
				Corn	GIFT	VELE
0.0175	-	-	-	0	0	80
"	8.96	-	-	45	80	80
"	"	29	4.48	40	75	85
"	"	4	8.96	10	65	70
"	"	5	"	20	70	80
"	"	77	"	55	85	60
"	"	30	4.48	10	90	95
"	"	7	8.96	30	80	85
"	"	12	4.48	5	75	70
"	"	15	8.96	15	85	85
"	"	24	4.48	50	85	85
"	"	31	"	40	85	80
"	"	32	"	50	80	90
"	"	33	"	15	75	80
"	"	2	"	25	80	80
"	"	6	"	30	80	85
"	"	8	"	20	85	80
"	"	10	"	20	75	90

Example 23

This test was conducted simultaneously with that in Example 22, except using THIMET 20G as the biocidal component. Test results are shown in Table 22.

Table 22 (continued)

Herbicide No. 1 (Kg/Ha)	Biocide No. 10 (Kg/Ha)	Antidote No.	Rate (Kg/Ha)	% Inhibition		
				Corn	GIFT	VELE
0.0175	8.96	16	4.48	25	55	85
"	"	20	"	10	75	90
"	"	23	"	5	60	90
"	"	1	"	15	65	95
-	"	-	-	5	30	15

Table 23

Herbicide No. 21 (Kg/Ha)	Biocide No. 1 (Kg/Ha)	Antidote No.	Rate (Kg/Ha)	% Inhibition		
				Corn	GIFT	VELE
0.0175	-	-	-	0	0	60
"	8.96	-	-	50	60	70
"	"	29	4.48	40	65	65
"	"	4	8.96	35	60	70
"	"	5	"	5	20	50
"	"	77	"	15	70	70
"	"	30	4.48	55	80	90
"	"	7	8.96	30	70	75
"	"	12	4.48	0	55	60
"	"	15	8.96	15	70	75
"	"	24	4.48	45	70	60
"	"	31	"	50	75	70
"	"	32	"	40	60	65
"	"	33	"	10	50	65
"	"	2	"	40	70	75
"	"	6	"	30	55	60
"	"	8	"	25	50	55
"	"	10	"	20	60	80

Example 25

The test reported in this example was a duplicate of that in the preceding example, but for substitution of DYFONATE 10G as the biocidal component. The test data for this example is shown in Table 24.

Table 24 (continued)

Herbicide No. 21 (Kg/Ha)	Biocide No. 9 (Kg/Ha)	Antidote No.	Rate (Kg/Ha)	% Inhibition		
				Corn	GIFT	VELE
0.0175	8.96	16	4.48	15	75	80
"	"	20	"	20	75	75
"	"	23	"	5	65	70
"	"	1	"	20	60	65
-	"	-	-	0	30	0

[1] "ND" indicates test yielded no meaningful data for one reason or another.

Table 25

Herbicide No. 21 (Kg/Ha)	Biocide No. 2 (Kg/Ha)	Antidote No.	Rate (Kg/Ha)	% Inhibition Corn	GIFT	VELE
0.0175	-	-	-	0	0	60
"	8.96	-	-	55	90	70
"	"	29	4.48	60	95	95
"	"	4	8.96	45	90	75
"	"	5	"	40	90	70
"	"	77	"	35	95	80
"	"	30	4.48	60	95	100
"	"	7	8.96	45	95	80
"	"	12	4.48	25	90	70
"	"	15	8.96	20	95	90
"	"	24	4.48	55	90	70
"	"	31	"	60	95	70
"	"	32	"	60	90	60
"	"	33	"	15	95	70
"	"	2	"	45	90	75
"	"	6	"	40	90	80
"	"	8	"	45	90	80
"	"	10	"	50	95	75

Example 27

This test was conducted simultaneously with that in Example 22, except using THIMET 20G as the biocidal component. Test results are shown in Table 26.

Table 26 (continued)

Herbicide No. 21 (Kg/Ha)	Biocide No. 10 (Kg/Ha)	Antidote No.	Rate (Kg/Ha)	% Inhibition		
				Corn	GIFT	VELE
0.0175	8.96	16	4.48	20	60	70
"	"	20	"	10	60	70
"	"	23	"	5	55	70
"	"	1	"	0	55	75
-	"	-	-	0	20	20

Table 27

Herb. No. (0.14 kg/Ha)	COUNTER® 15G (Kg/Ha)	Antidote No.	Rate (Kg/Ha)	% Inhibition Corn	GIFT	VELE
1	-	-	-	10	30	95
"	8.96	-	-	70	90	85
"	"	12	4.48	0	80	100
"	"	1	"	5	85	90
"	"	28	"	5	80	90
21	-	-	-	5	40	75
"	8.96	-	-	75	95	80
"	"	12	4.48	20	85	90
"	"	1	"	10	90	90
"	"	28	"	35	90	90
-	8.96	-	-	0	0	0

Table 28

Herbicide No.	COUNTER® 15G (Kg/Ha)	Antidote No.	Rate (Kg/Ha)	% Inhibition Corn	SHCA	VELE
8	-	-	-	5	80	85
"	8.96	-	-	60	85	85
"	"	12	4.48	0	80	90
"	"	1	"	15	75	85
"	"	28	"	20	75	85
7	-	-	-	0	75	70
"	8.96	-	-	55	75	75
"	"	12	4.48	20	80	80
"	"	1	"	30	75	80
"	"	28	"	35	75	75
18	-	-	-	5	20	65
"	8.96	-	-	55	30	70
"	"	12	4.48	25	25	75
"	"	1	"	25	20	70
"	"	28	"	45	25	70
-	8.96	-	-	0	20	0

Table 29

BEACON® (Kg/Ha)	COUNTER® 15G (Kg/Ha)	Antidote No.	Rate (Kg/Ha)	% Inhibition Corn	SHCA	VELE
0.07	-	-	-	0	75	80
"	8.96	-	-	70	75	85
"	"	22	4.48	20	65	85
"	"	1	"	10	70	90
"	"	34	"	15	70	85
"	"	35	"	20	75	90
"	"	36	"	45	75	100
"	"	27	"	25	75	85
"	"	37	"	65	80	90
"	"	38	"	20	80	95
"	"	13	"	30	70	85
"	"	14	"	10	80	90
"	"	39	"	25	75	90
"	"	40	"	45	85	90
"	"	26	"	40	70	90
"	"	41	"	25	80	90
"	"	3	"	35	70	95
"	"	17	"	15	75	95
"	"	18	"	55	70	85

Example 31

This test was conducted simultaneously with that in Example 30 under the same conditions, except using PURSUIT as the herbicidal component. Test results are shown in Table 30.

Table 30 (continued)

PURSUIT® 15G (Kg/Ha)	COUNTER® Antidote (Kg/Ha)	Rate No.	(Kg/Ha)	% Inhibition Corn	SHCA	VELE
0.07	8.96	17	"	30	45	75
"	"	18	"	50	20	70
"	"	19	"	35	30	70
"	"	21	"	40	30	70
"	"	25	"	50	45	70
-	8.96	-	-	5	10	0

Table 31

XRD-498 (Kg/Ha)	COUNTER® 15G (Kg/Ha)	Antidote No.	Rate (Kg/Ha)	% Inhibition Corn	% Inhibition GIFT	% Inhibition VELE
0.02	-	-	-	5	30	80
"	8.96	-	-	70	75	80
"	"	22	4.48	45	70	80
"	"	1	"	25	70	85
"	"	34	"	35	75	80
"	"	35	"	40	70	80
"	"	36	"	60	75	90
"	"	27	"	30	75	85
"	"	37	"	60	80	85
"	"	38	"	50	70	85
"	"	13	"	65	80	90
"	"	14	"	45	75	90
"	"	39	"	50	85	95
"	"	40	"	60	70	85
"	"	26	"	65	75	80
"	"	41	"	60	90	80
"	"	3	"	55	75	95

Example 33

This example was conducted according to the identical procedure described in Example 30, except that a different series of Antidotal compounds was used in this example to evaluate the negative synergy developed from the interaction of BEACON® herbicide and COUNTER® 15G insecticide. The herbicide was applied POE six (6) days after PPI application of the insecticide. Observations were made eight (8) days later. Test results are shown in Table 32.

Table 32 (Continued)

BEACON® (Kg/Ha)	COUNTER® 15G (Kg/Ha)	Antidote No.	Rate (Kg/Ha)	% Inhibition Corn	SHCA	VELE
0.07	8.96	55	"	25	75	85
"	"	56	"	60	75	85
"	"	57	"	15	80	85
"	"	58	"	55	70	85
"	"	59	"	15	80	85
-	8.96	-	-	0	0	0

Table 33

PURSUIT® (Kg/Ha)	COUNTER® 15G (Kg/Ha)	Antidote No.	Rate (Kg/Ha)	% Inhibition		
				Corn	SHCA	VELE
0.01	-	-	-	5	30	70
"	8.96	-	-	65	30	70
"	"	12	4.48	40	40	75
"	"	42	"	60	30	70
"	"	43	"	65	35	75
"	"	44	"	60	30	65
"	"	45	"	65	25	70
"	"	46	"	55	25	70
"	"	80	"	55	35	75
"	"	47	"	50	30	75
"	"	48	"	45	25	70
"	"	49	"	70	30	80
"	"	50	"	45	25	70
"	"	51	"	30	35	70
"	"	52	"	45	25	75
"	"	53	"	50	25	70
"	"	54	"	55	20	65

Example 35

The example was conducted according to the PPI procedure described in Procedure IV above. The herbicidal component in this example was XRD-498 Herbicide No. 21. Observations of plant response made fourteen (14) days after PPI of chemicals. Test results are shown in Table 34.

Table 34 (Continued)

XRD-498 (Kg/Ha)	COUNTER® 15G (Kg/Ha)	Antidote No.	Rate (Kg/Ha)	% Inhibition Corn	GIFT	VELE
0.02	8.96	55	"	45	65	90
"	"	56	"	65	75	85
"	"	19	"	35	65	90
"	"	57	"	65	70	80
"	"	58	"	30	60	90
-	8.96	59	-	0	30	20

Table 35

BEACON® (Kg/Ha)	COUNTER® 15G (Kg/Ha)	Antidote No.	Rate (Kg/Ha)	% Inhibition Corn	SHCA	VELE
0.07	-	-	-	0	65	75
"	8.96	-	-	70	75	80
"	"	60	8.96	40	60	80
"	"	61	"	35	65	75
"	"	62	"	30	65	80
"	"	63	"	30	70	80
"	"	64	"	20	65	75
"	"	65	"	25	70	80
"	"	7	"	20	65	75
"	"	66	"	30	60	80
"	"	67	"	35	65	85
"	"	68	"	25	70	85
"	"	69	"	30	75	80
"	"	70	"	70	70	90
"	"	9	"	15	70	90
"	"	11	"	25	75	80
"	"	71	"	20	65	85

Example 37

The identical procedure in Example 36 was conducted simultaneously with this test, except for use of the herbicide PURSUIT here. Results are shown in Table 36.

Table 36 (Continued)

PURSUIT® (Kg/Ha)	COUNTER® 15G (Kg/Ha)	Antidote No.	Rate (Kg/Ha)	% Inhibition Corn	SHCA	VELE
0.01	8.96	72	4.48	60	30	70
"	"	73	"	70	35	70
"	"	74	"	60	20	70
"	"	75	"	65	40	75
"	"	76	"	55	30	70
-	8.96	-	-	0	10	10

Table 37

XRD-498 (Kg/Ha)	COUNTER® 15G (Kg/Ha)	Antidote No.	Rate (Kg/Ha)	% Inhibition Corn	GIFT	VELE
0.02	-	-	-	15	25	90
"	8.96	-	-	75	70	90
"	"	60	8.96	60	75	90
"	"	61	"	60	70	90
"	"	62	"	65	75	95
"	"	63	"	65	70	90
"	"	64	"	60	70	90
"	"	65	"	45	70	90
"	"	7	"	55	80	85
"	"	66	"	50	70	90
"	"	67	"	55	75	95
"	"	68	"	45	65	80
"	"	69	"	35	70	90
"	"	70	"	75	70	95
"	"	9	"	20	95	100
"	"	11	"	25	70	90
"	"	71	"	30	70	90

The data in Tables 29-37 show that corn injury was increased from 0-5% to 55-70% when COUNTER was used in conjunction with BEACON, PURSUIT or XRD-498. The dichloroacetamide antidotes tested in Examples 3-37 (Tables 29-31) were more effective in BEACON than with PURSUIT and XRD-498. MON-13900 was the most active antidote in these tests followed by Antidote Nos. 27 and 34. In summary, nineteen of twenty of the tested dichloroamide antidotes exhibited significant safening activity, again, led by MON-13900. Significant activity was also shown by seventeen of twenty benzhydryl-class antidotes, of which Antidote No. 51 was most active closely followed by MON-7400. Of ten antidotes of thiazole chemistry all ten were active against negative synergism, with fluazole (No. 7) and Antidote No. 65 being slightly more active than other thiazoles tested. Other active safeners included the oxime Antidote No. 9 (cyometrinil) and the oxazole Antidote No. 11, against PURSUIT/COUNTER interactions.

In further tests to evaluate the applications of this invention, another series of tests were conducted to evaluate the antidotal efficacy of various representative antidotes in combating negative synergy induced by a diverse variety of herbicidal compounds used or expected to be used in loci previously treated with biocides to control various crop pests. In this series of tests, COUNTER 15 G was used because of its prevalent use in agriculture. These tests are described in Examples 39-50 below, using procedures described in Procedures VI and VII described above.

Table 38

Herbicide No.	Rate (Kg/Ha)	Biocide No.		Antidote No.	% Inhibition Corn	% Inhibition GIFT	% Inhibition VELE
1	0.14	-		-	0	0	85
"	"	1		-	35	0	90
"	"	1	+	12	0	0	90
"	"	1	+	7	5	0	90
"	"	1	+	1	15	0	95
"	"	1	+	33	0	0	90
10	0.002	-		-	15	0	90
"	"	1		-	55	0	85
"	"	1	+	12	5	0	90
"	"	1	+	7	10	20	85
"	"	1	+	1	15	0	90
"	"	1	+	33	5	0	90
4	0.17	-		-	0	0	80
"	"	1		-	45	0	85
"	"	1	+	12	0	0	85
"	"	1	+	7	0	0	85
"	"	1	+	1	10	0	90
"	"	1	+	33	5	0	90

Table 39

Herbicide No.	Rate (Kg/Ha)	Biocide No.		Antidote No.	% Inhibition Corn	GIFT	VELE
5	0.07	-		-	5	0	85
"	"	1		-	75	0	90
"	"	1	+	12	0	0	85
"	"	1	+	7	55	0	90
"	"	1	+	1	15	0	95
"	"	1	+	33	30	0	90
7	0.56	-		-	0	85	70
"	"	1		-	60	85	65
"	"	1	+	12	5	85	75
"	"	1	+	7	25	85	70
"	"	1	+	1	10	85	75
"	"	1	+	33	10	80	65
15	0.0044	-		-	0	0	75
"	"	1		-	30	0	75
"	"	1	+	12	0	0	75
"	"	1	+	7	10	0	75
"	"	1	+	1	10	20	75
"	"	1	+	33	15	0	80

Table 40

Herbicide No.	Rate (Kg/Ha)	Biocide No.		Antidote No.	% Inhibition Corn	% Inhibition GIFT	% Inhibition VELE
16	0.01	-		-	50	20	30
"	"	1		-	70	15	40
"	"	1	+	12	15	20	25
"	"	1	+	7	30	10	30
"	"	1	+	1	20	35	35
"	"	1	+	33	30	30	40
19	0.28	-		-	5	45	70
"	"	1		-	35	40	60
"	"	1	+	12	0	35	60
"	"	1	+	7	10	40	70
"	"	1	+	1	20	35	65
"	"	1	+	33	10	35	60
6	0.01	-		-	5	50	60
"	"	1		-	65	55	65
"	"	1	+	12	0	50	65
"	"	1	+	7	45	45	70
"	"	1	+	1	15	60	60
"	"	1	+	33	20	65	65

The above data in Table 40 show that the test antidotes all reduced negative synergy induced by the interaction of the imidazolinone herbicides when contacted with COUNTER 15G insecticide. As in preceding tests, MON-7400 was the most efficacious antidote for these negative synergy interactions.

Example 42

This example describes the testing of the above antidotes used in Examples 39-41 to safen negative synergy interactions between representative species of the class of herbicidal compounds identified as azolopyrimidine sulfonamides and COUNTER 15G. The same procedure used in the above examples was conducted in this test. In this test, the herbicides were formulated in 17% acetone and 83% water with 0.25% v/v X-77 surfactant. Test data are shown in Table 41.

In the data in Table 41 it is shown that negative synergy developed between COUNTER 15G and the sulfonamide herbicides significantly enhance corn injury. Also, this injury was significantly reduced by in-furrow treatments with MON-7400, flurazole, MON-13900 and Antidote No. 33. Once again, MON-7400 (No. 12) was the most effective safener and provided 92-100% safening of corn injury.

Example 43

In continuing tests to evaluate the variations of this invention, a series of tests were conducted to determine the efficacy of the above safeners in Examples 39-42 to alleviate corn injury induced by the interaction of various additional commercial sulfonylurea herbicides with COUNTER 15G insecticide. In this example, the tests were conducted according to Procedure VI above. In modifications of that procedure, herbicides were applied to soil samples as acetone/water suspensions, incorporated by shaking in a closed container, with subsamples used to cover furrow-treated 10.2 cm pots. Pots were subirrigated followed by overhead misting on days 6-10. Test data (average of two reps) are shown in Table 42.

Table 42 (continued)

Herbicide No.	Rate (Kg/Ha)	Biocide No.		Antidote No.	% Inhibition Corn	GIFT	VELE
11	0.0044	-		-	10	0	70
"	"	1		-	50	0	65
"	"	1	+	12	10	0	70
"	"	1	+	7	15	0	65
"	"	1	+	1	15	0	75
"	"	1	+	33	20	0	65

Table 43

Herbicide No.	Rate (Kg/Ha)	Biocide No.		Antidote No.	% Inhibition Corn	GIFT	VELE
16	0.07	-		-	45	40	70
"	"	1		-	65	45	65
"	"	1	+	12	40	35	60
"	"	1	+	7	55	50	60
"	"	1	+	1	45	30	60
"	"	1	+	33	35	45	65
17	0.14	-		-	15	80	80
"	"	1		-	55	80	75
"	"	1	+	12	10	80	80
"	"	1	+	7	35	75	80
"	"	1	+	1	45	75	80
"	"	1	+	33	20	80	75
18	0.04	-		-	10	60	65
"	"	1		-	25	50	60
"	"	1	+	12	5	50	70
"	"	1	+	7	10	65	45
"	"	1	+	1	10	55	50
"	"	1	+	33	5	45	40

Table 44

Herbicide No.	Rate (Kg/Ha)	Biocide No.		Antidote No.	% Inhibition Corn	GIFT	VELE
20	1.12	-		-	25	15	95
"	"	1		-	55	20	95
"	"	1	+	12	25	25	95
"	"	1	+	7	35	10	95
"	"	1	+	1	25	20	95
"	"	1	+	33	50	30	90
22	0.28	-		-	0	10	80
"	"	1		-	60	25	75
"	"	1	+	12	0	20	75
"	"	1	+	7	15	25	80
"	"	1	+	1	5	25	80
"	"	1	+	33	5	15	90
24	0.14	-		-	35	10	90
"	"	1		-	65	10	95
"	"	1	+	12	30	20	90
"	"	1	+	7	30	15	95
"	"	1	+	1	25	10	90
"	"	1	+	33	40	25	95

Table 45

Herbicide No.	Rate (Kg/Ha)	Biocide No.		Antidote No.	% Inhibition Corn	GIFT	VELE
25	0.14	-		-	20	30	70
"	"	1		-	85	35	70
"	"	1	+	12	0	25	70
"	"	1	+	7	5	20	75
"	"	1	+	1	15	30	75
"	"	1	+	33	20	25	70
26	2.24	-		-	0	0	40
"	"	1		-	20	0	65
"	"	1	+	12	5	0	55
"	"	1	+	7	5	10	70
"	"	1	+	1	20	0	65
"	"	1	+	33	10	15	50
28	0.04	-		-	20	25	80
"	"	1		-	70	50	85
"	"	1	+	12	10	35	80
"	"	1	+	7	55	45	90
"	"	1	+	1	20	50	90
"	"	1	+	33	30	40	80

Table 46

Herbicide No.	Rate (Kg/Ha)	Biocide No.		Antidote No.	% Inhibition Corn	GIFT	VELE
6	0.14	-		-	5	75	65
"	"	1		-	60	70	70
"	"	1	+	12	10	60	65
"	"	1	+	7	40	60	60
"	"	1	+	1	15	65	70
"	"	1	+	33	20	70	70
13	0.0011	-		-	30	0	20
"	"	1		-	65	10	25
"	"	1	+	12	35	0	15
"	"	1	+	7	50	0	10
"	"	1	+	1	40	25	25
"	"	1	+	33	40	10	20

Table 47

Herbicide No. 8 (Kg/Ha)	Antidote No.	% Corn Inhibition		C:A Ratios					
		None	C	5	10	20	40	80	160
0.28	8	0	24	3	5	5	3	5	10
"	51	0	25	0	5	3	8	10	10
"	16	1	26	3	10	10	15	28	23
"	1	0	18	3	3	0	0	3	13

Weed Control (separate 10.2 cm pots)

	% Inhibition
GIFT	65
SHCA	70
VELE	80

Table 48

BEACON® (Kg/Ha)	In-Furrow Treatment C ± A	C:A Ratio	% Inhibition Corn
0.28	-	-	0
"	C	-	55
0.28	C + 78	20	5
"	"	40	5
"	"	80	20
"	"	160	20
0.28	C + 79	20	0
"	"	40	5
"	"	80	15
"	"	160	20
0.28	C + 8	20	0
"	"	40	0
"	"	80	5
"	"	160	15

Example 50

The above test was simultaneously duplicated procedurally, except using ACCENT® (Herbicide No. 7) as the herbicide; antidotes were the same as well as the insecticide. Test results are shown in Table 49.

Table 49 (continued)

BEACON® (Kg/Ha)	In-Furrow Treatment C + A	C:A Ratio	% Inhibition Corn
0.56	C + 16	20	35
"	"	40	40
"	"	80	35
"	"	160	40
0.56	C + 1	20	10
"	"	40	10
"	"	80	10
"	"	160	15
0.56	C + 28	20	15
"	"	40	15
"	"	80	20
"	"	160	15
-	C	-	0

Weed inhibition in this test was follows: GIFT, 95%, SHCA, 95%, VELE, 90%.

Table 50

Herbicide No.	Rate (Kg/Ha)	Biocide No. 8 (kg/Ha)	Antidote No.	Rate (Kg/Ha)	% Inhibition Corn	SHCA	VELE
8	0.28	-	-	-	5	80	90
"	"	8.96	-	-	25	90	90
"	"	"	7	4.48	35	100	95
"	"	"	12	"	30	100	90
"	"	"	16	"	25	100	90
"	"	"	1	"	60	100	95
"	"	"	33	"	30	100	85
"	"	"	28	"	35	100	90
7	0.56	-	-	-	10	75	80
"	"	8.96	-	-	30	95	85
"	"	"	7	4.48	40	100	85
"	"	"	12	"	35	100	90
"	"	"	16	"	45	100	90
"	"	"	1	"	55	100	85
"	"	"	33	"	30	100	90
"	"	"	28	"	40	95	90

In this test MOCAP alone at 8.96 kg/ha produced corn stunting, leaf malformations and stand loss; these manifestations of injury were predominant in this test. No interactions or safening effects were observed between BEACON, ACCENT or PURSUIT under conditions of this test. This is not unexpected as the phenomenon of negative synergy can be capricious, depending upon many factors, e.g., climatic, edaphic, etc., as further exemplified by the varied results involving test evaluations of reported corn injury by ERADICANE® (EPTC + dichlormid) or SURPASS® and fonofos in the Canadian Journal of Plant Science, supra. As the authors concluded: results of tests involving negative can be inconsistent from year to year.

Example 52

The test in this example paralleled that in Example 51, except the procedure was according to Procedure IV above and the herbicides used were No. 1 (MON-12000); No. 21 (XRD-498) and, again, No. 18 (PURSUIT); the biocide was, again, MOCAP®. Observations were taken thirteen (13) days after PPI treatment with biocide and antidote. Results are shown in Table 51.

Table 51 (continued)

Herbicide No.	Rate (Kg/Ha)	Biocide No. 8 (kg/Ha)	Antidote No.	Rate (Kg/Ha)	% Inhibition Corn	GIFT	VELE
18	0.14	-	-	-	15	75	65
"	"	8.96	-	-	60	100	75
"	"	"	7	4.48	70	100	80
"	"	"	12	"	50	95	65
"	"	"	16	"	60	100	75
"	"	"	1	"	55	100	75
"	"	"	33	"	50	100	80
"	"	"	28	"	50	100	80
-	-	8.96	-	-	30	90	20

Table 52

Herbicide No.	Rate (Kg/Ha)	Biocide No. 5 (kg/Ha)	Antidote No.	Rate (Kg/Ha)	% Inhibition Corn	SJCA	VELE
1	0.14	-	-	-	0	70	85
"	"	8.96	-	-	65	95	85
"	"	"	7	4.48	10	95	90
"	"	"	12	"	5	95	95
"	"	"	16	"	0	95	85
"	"	"	1	"	0	95	90
"	"	"	33	"	15	95	90
"	"	"	28	"	5	100	95
21	0.14	-	-	-	5	70	80
"	"	8.96	-	-	35	90	80
"	"	"	7	4.48	15	95	85
"	"	"	12	"	0	90	80
"	"	"	16	"	40	95	85
"	"	"	1	"	5	95	85
"	"	"	33	"	15	90	80
"	"	"	28	"	5	90	85

In this test corn injury was seen with all biocide/herbicide combinations. Effective safening occurred with most combinations, especially those with MON-7400 (No. 12), MON-13900 (No. 1) and CGA 154281 (No. 28).

Example 54

This test was also identical to that in the preceding two examples, except that the biocide was malathion (No. 7, an insecticide). Test results shown in Table 53.

Table 53 (continued)

Herbicide No.	Rate (Kg/Ha)	Biocide No. 7 (kg/Ha)	Antidote No.	Rate (Kg/Ha)	% Inhibition Corn	GIFT	VELE
18	0.14	-	-	-	15	70	75
"	"	8.96	-	-	50	90	75
"	"	"	7	4.48	0	80	65
"	"	"	12	"	0	90	75
"	"	"	16	"	20	80	75
"	"	"	1	"	5	85	70
"	"	"	33	"	25	85	75
"	"	"	28	"	0	80	70
-	-	8.96	-	-	0	0	0

Table 54

Herbicide No.	Rate (Kg/Ha)	Biocide No. 6 (kg/Ha)	Antidote No.	Rate (Kg/Ha)	% Inhibition Corn	SJCA	VELE
1	-	-	-	-	5	65	90
"	"	8.96	-	-	55	75	95
"	"	"	7	4.48	10	90	95
"	"	"	12	"	15	80	90
"	"	"	16	"	25	75	90
"	"	"	1	"	10	80	95
"	"	"	33	"	15	80	90
"	"	"	28	"	15	75	90
21	0.14	-	-	-	10	60	85
"	"	8.96	-	-	60	80	80
"	"	"	7	4.48	25	85	85
"	"	"	12	"	0	75	80
"	"	"	16	"	25	85	85
"	"	"	1	"	5	85	85
"	"	"	33	"	10	85	90
"	"	"	28	"	15	80	85

Onc again, the t st saf ners all provided moderate to high degrees of safening activity against interactions from combinations of FORTRESS with MON-12000 and XRD-498. With the exception of MON-7400, these antidotes were less effective against the FORTRESS/PURSUIT interaction.

In another series of tests of the multiple variations of this invention, various herbicidal and co-herbicidal combinations were tested to evaluate the antidotal effectiveness of selected antidotes against corn injury by negative synergism induced by the interaction of said herbicidal/co-herbicidal mixtures and a biocide, exemplified by COUNTER® 15G. Test procedures in this series followed either Procedure VI or VII described above with noted variations. In the tables below COUNTER® 15G is symbolized by the letter "C" and the antidotes by the letter "A".

Example 56

In the first test in this series of tests with co-herbicides, was conducted according to general Procedure VII described above, wherein the in-furrow treatments involving biocide/safener incorporation comprised granules of COUNTER 15G alone or blended in a 50:50 mix with safener 15G at 7.4 + 7.4 mg/cm or 1.1 + 0.37 mg active ingredient/cm.

The herbicide was BEACON® (No. 8) in combination with co-herbicides H (2,4-D); F (BANVEL®); G (BLADEX®); I (MON-12000) or J (XRD-498). BEACON and XRD-498 were formulated in 50% water/50% acetone containing 0.25 v/v% of X-77 surfactant. The POE combinations were applied as tank mixtures, five (5) days after the PPI operation and plant response observations taken eight (8) days later. Test results are shown in Table 55.

Table 55 (continued)

Herbicide No.	+	Co-Herbicide	Rate (Kg/Ha)	C ± A	% Inhibition Corn	SHCA	VELE
8	+	I	0.14 + 0.07	-	0	75	90
"	"	"	" " "	C	20	70	90
"	"	"	" " "	C + 12	10	70	90
"	"	"	" " "	C + 7	0	70	90
"	"	"	" " "	C + 1	10	75	90
"	"	"	" " "	C + 16	5	70	95
8	+	J	0.28 + 0.07	-	0	70	85
"	"	"	" " "	C	70	80	85
"	"	"	" " "	C + 12	10	75	90
"	"	"	" " "	C + 7	40	75	90
"	"	"	" " "	C + 1	20	80	90
"	"	"	" " "	C + 16	15	75	85

Table 56

Herbicide No.	+	Co-Herbicide	Rate (Kg/Ha)	C ± A	% Inhibition Corn	SHCA	VELE
7	+	H	0.28 + 0.28	-	15	70	80
"	"	"	" " "	C	25	60	85
"	"	"	" " "	C + 12	10	70	80
"	"	"	" " "	C + 7	10	75	85
"	"	"	" " "	C + 1	10	70	80
"	"	"	" " "	C + 16	15	75	80
7	+	F	0.28 + 0.28	-	5	75	85
"	"	"	" " "	C	30	60	80
"	"	"	" " "	C + 12	5	80	85
"	"	"	" " "	C + 7	20	70	80
"	"	"	" " "	C + 1	5	65	85
"	"	"	" " "	C + 16	10	70	85
7	+	G	0.28 + 1.12	-	10	70	95
"	"	"	" " "	C	20	55	100
"	"	"	" " "	C + 12	5	65	100
"	"	"	" " "	C + 7	15	65	100
"	"	"	" " "	C + 1	15	70	100
"	"	"	" " "	C + 16	15	75	95

In this example corn injury was r duced by in-furrow treatments of all herbicide/co-herbicide combinations applied POE and in contact with COUNTER 15G with all test antidotes.

Example 58

This example describes a process substantially identical to that in Examples 56 and 57, except using PURSUIT® (Herbicide No. 18) as the herbicide. The co-herbicides, biocide and safeners are shown in Table 57, together with test results.

Table 57 (continued)

Herbicide No.	+	Co-Herbicide	Rate (Kg/Ha)	C ÷ A	% Inhibition Corn	% Inhibition SHCA	% Inhibition VELE
18	+	I	0.01 + 0.07	-	15	25	0-
"	"	"	" " "	C	75	2-	0-
"	"	"	" " "	C + 12	15	25	0-
"	"	"	" " "	C + 7	30	30	90
"	"	"	" " "	C + 1	25	3-	05
"	"	"	" " "	C + 16	35	35	05
18	+	J	0.01 + 0.07	-	15	20	85
"	"	"	" " "	C	70	25	90
"	"	"	" " "	C + 12	25	30	90
"	"	"	" " "	C + 7	60	25	90
"	"	"	" " "	C + 1	45	35	85
"	"	"	" " "	C + 16	55	25	90

Table 58

Herbicide No.	+	Co-Herbicide	Rate (Kg/Ha)	C ± A	% Inhibition Corn	GIFT	VELE
1	+	B	0.14 + 0.56	-	40	100	100
"	"	"	" " "	C	85	99	100
"	"	"	" " "	C + 12	0	95	100
"	"	"	" " "	C + 7	15	95	100
"	"	"	" " "	C + 1	10	95	95
"	"	"	" " "	C + 16	5	99	100
1	+	C	0.14 + 0.4	-	20	99	95
"	"	"	" " "	C	70	95	95
"	"	"	" " "	C + 12	0	95	95
"	"	"	" " "	C + 7	0	95	100
"	"	"	" " "	C + 1	10	99	100
"	"	"	" " "	C + 16	15	99	100
1	+	A	0.14 + 0.28	-	35	99	100
"	"	"	" " "	C	05	00	100
"	"	"	" " "	C + 12	20	95	100
"	"	"	" " "	C + 7	10	95	100
"	"	"	" " "	C + 1	15	100	100
"	"	"	" " "	C + 16	15	99	100

The above test data show that the tested safeners each provided high levels of corn safening against the negative synergy developed by contact of the herbicide/co-herbicide mixtures with COUNTER 15G.

Example 60

This test was conducted in the same manner used in Example 59. All biocide and antidote components were the same and in these tests XRD-498 (Herbicide No. 21) was the prime herbicide. Co-herbicides are shown in Table 59 together with test data.

Table 59 (continued)

Herbicide N.	+	Co-Herbicide	Rate (Kg/Ha)	C ⁺ A	% Inhibition Corn	SHCA	VELE
21	+	D	0.14 + 2.24	-	5	90	100
"	"	"	" " "	C	65	95	95
"	"	"	" " "	C + 12	0	95	100
"	"	"	" " "	C + 7	30	90	100
"	"	"	" " "	C + 1	15	95	95
"	"	"	" " "	C + 16	10	90	100
21	+	E	0.14 + 2.24	-	0	95	95
"	"	"	" " "	C	55	99	90
"	"	"	" " "	C + 12	10	99	95
"	"	"	" " "	C + 7	30	99	90
"	"	"	" " "	C + 1	20	95	90
"	"	"	" " "	C + 16	25	99	90
21	+	K	0.14 + 0.07	-	10	60	90
"	"	"	" " "	C	65	55	85
"	"	"	" " "	C + 12	10	60	80
"	"	"	" " "	C + 7	30	50	85
"	"	"	" " "	C + 1	25	60	85
"	"	"	" " "	C + 16	35	65	90

Table 60

Herbicide No.	+	Co-Herbicide	Rate (Kg/Ha)	C * A	% Inhibition Corn	% Inhibition SHCA	% Inhibition VELE
18	+	B	0.14 + 0.56	-	40	100	80
"	"	"	" " "	C	75	100	85
"	"	"	" " "	C + 12	15	99	85
"	"	"	" " "	C + 7	55	99	80
"	"	"	" " "	C + 1	5	100	85
"	"	"	" " "	C + 16	20	95	90
18	+	C	0.14 + 0.4	-	20	99	75
"	"	"	" " "	C	65	99	80
"	"	"	" " "	C + 12	5	99	80
"	"	"	" " "	C + 7	25	99	85
"	"	"	" " "	C + 1	15	99	80
"	"	"	" " "	C + 16	20	99	80
18	+	A	0.14 + 0.28	-	50	100	90
"	"	"	" " "	C	85	100	80
"	"	"	" " "	C + 12	15	99	85
"	"	"	" " "	C + 7	65	99	85
"	"	"	" " "	C + 1	25	99	80
"	"	"	" " "	C + 16	20	100	80

In this test, c rn injury arising from the expected herbicide/biocide interaction was reduced by in-furrow applications of MON-7400, flurazole, MON-13900 or MON-4660. Of the safeners here, MON-7400 and MON-13900 were more effective than flurazole or MON-4660 in safening the negative synergy developed.

The above series of tests with various herbicide/co-herbicide combinations, safeners and a commercial biocide indicate the broad scope of this invention. In particular, it is to be noted that all of the above herbicides, except XRD-498, whether designated for purposes of illustration herein as the "prime" or "principal" herbicide or as a "co-herbicide" are commercial products. Thus, the importance of the invention is emphasized.

Moreover, the successful safening with a wide variety of antidotal compounds of negative synergy from a wide variety of herbicides, co-herbicides and biocides suggests the broad scope of the invention. Other products which may suitably be useful according to this invention are combinations of the herbicidal compound dicamba and its alkali metal salts or alkylamine or ammonium salts with any of the herbicides exemplified above as herbicides and/or co-herbicides, whether primarily suitable as graminaceous or broad leaf herbicides, e.g., alachlor, acetochlor, metolachlor, or other α-haloacetamides and α-haloacetanilides or other chemistries mentioned herein, further containing or contacted with any suitable antidote and biocide particularly those designated herein as preferred, e.g., COUNTER® insecticide, MON-7400, MON-13900, CGA-151284, etc., antidotes.

Tests according to this invention in various crops indicate widespread application of the invention. In Examples 62-66 below are described tests with a vari ty of herbicides contacted with COUNTER 15G in the pr sence and absence of MON-7400 (Antidote N . 12); MON-

Table 61

Herb. No. 8 Kg/Ha)	Biocide No. 1 (Kg/Ha)	Antidote No.	Rate (Kg/Ha)	% Inhibition COTT	SOBE	CORN	GRSO	WHEA	RICE	GIFT	VELE
0.14	-	-	-	70	55	0	80	70	80	80	95
"	8.96	-	-	65	50	35	80	70	80	85	95
"	"	12	4.48	65	60	0	85	65	70	80	90
"	"	7	"	70	55	5	85	70	80	90	95
"	"	1	"	65	40	5	80	65	75	80	95
"	"	16	"	70	60	0	80	65	80	85	95
0.17	-	-	-	65	45	0	75	60	70	65	95
"	8.96	-	-	70	45	10	70	75	70	80	95
"	"	12	4.48	65	40	5	70	70	65	75	95
"	"	7	"	60	40	0	75	70	65	70	95
"	"	1	"	60	40	0	75	60	60	75	95
"	"	16	"	65	45	5	70	60	60	85	90

Example 63

The test procedure described in Example 62 was repeated using ACCENT® (Herbicide No. 7) as the herbicide; the biocide and safeners were the same. Test results are shown in Table 62.

Table 62 (continued)

Herb. No. 7 Kg/Ha)	Biocide No. 1 (Kg/Ha)	Antidote No.	Rate (Kg/Ha)	% Inhibition COTT	SOBE	CORN	GRSO	WHEA	RICE	GIFT	VELE
0.0044	-	-	-	25	10	0	60	35	20	65	40
"	8.96	-	-	30	15	5	65	45	25	70	45
"	"	12	4.48	30	10	0	65	40	30	70	40
"	"	7	"	35	5	0	60	45	20	75	35
"	"	1	"	20	20	0	65	45	15	60	40
"	"	16	"	20	20	0	65	50	20	70	50
-	"	-	-	0	0	0	0	0	20	20	25

Table 63

Herb. No. 18 Kg/Ha)	Biocide No. 1 (Kg/Ha)	Antidote No.	Rate (Kg/Ha)	% Inhibition							
				COTT	SOBE	CORN	GRSO	WHEA	RICE	GIFT	VELE
0.14	-	-	-	50	10	40	75	35	60	80	100
"	8.96	-	-	55	15	75	75	40	65	85	100
"	"	12	4.48	45	10	65	75	30	60	85	95
"	"	7	"	50	15	70	80	45	70	90	95
"	"	1	"	50	15	65	70	35	65	85	95
"	"	16	"	50	20	70	75	25	65	90	100
0.035	-	-	-	45	10	25	65	20	45	80	95
"	8.96	-	-	45	5	70	70	35	40	85	95
"	"	12	4.48	45	5	60	75	10	35	80	85
"	"	7	"	40	10	55	70	10	35	90	90
"	"	1	"	45	10	50	65	20	35	85	90
"	"	16	"	50	15	50	70	25	40	90	90

In the above Tables 61-63, it can be noted that interactions occurred between COUNTER 15G and BEACON in corn and wheat. Corn injury was effectively reduced by MON-7400, flurazole, MON-13900 and Antidote No. 33. The weak interaction effect on wheat was reduced slightly by these safeners.

The negative synergy between COUNTER and ACCENT was specific to corn and the resulting enhanced injury was corrected by the antidotes.

COUNTER and PURSUIT interacted negatively at one or more application rates to cause enhanced injury in corn, wheat and rice. Slight to moderate safening of corn was observed. Safening of weak interactions in wheat and rice ranged from slight to nil, depending on the antidote.

Example 65

In another test in the several crops and weeds used in this test series, the herbicidal component was MON-12000 (No. 1); the other components were the same. the procedure used in this test was the same as that described in Example 62, modified to use a light overhead irrigation (about 0.32 cm/day) during days 4-7 of the test. Results are shown in Table 64.

Table 64 (continued)

Herb. No. 1 Kg/Ha)	Biocide No. 1 (Kg/Ha)	Antidote No.	Rate (Kg/Ha)	% Inhibition COTT	SOBE	CORN	GRSO	WHEA	RICE	GIFT	VELE
0.018	-	-	-	10	15	0	0	0	0	0	70
"	8.96	-	-	15	5	0	0	0	0	70	75
"	"	12	4.48	10	5	0	0	0	0	30	50
"	"	7	"	25	10	0	0	0	10	80	60
"	"	1	"	20	35	5	0	0	0	50	65
"	"	16	"	30	10	0	0	25	10	75	75
-	"	-	-	0	0	0	0	0	10	30	0

Table 65

Herb. No. 1 Kg/Ha)	Biocide No. 1 (Kg/Ha)	Antidote No.	Rate (Kg/Ha)	% Inhibition COTT	SOBE	CORN	GRSO	WHEA	RICE	GIFT	VELE
0.28	-	-	-	40	20	10	80	0	60	70	90
"	8.96	-	-	75	15	75	85	85	90	90	90
"	"	12	4.48	35	15	20	55	20	70	85	85
"	"	7	"	60	5	40	70	30	70	95	90
"	"	1	"	45	5	20	65	70	95	95	90
"	"	16	"	40	10	25	85	25	85	90	95
0.07	-	-	-	20	0	0	40	0	40	60	80
"	8.96	-	-	20	0	0	20	0	25	65	80
"	"	12	4.48	10	0	0	20	0	20	80	75
"	"	7	"	0	0	10	30	25	30	60	65
"	"	1	"	20	0	5	25	25	25	80	75
"	"	16	"								

The tests in Examples 65 and 66 sh wed that increased injury to corn and wheat occurred as a result of the interaction between COUNTER 15G and MON-12000. All four safeners provided good protection against corn injury. With the exception of Antidote No. 33, the test antidotes showed good wheat safening.

The combination of COUNTER 15G with the sulfonamide herbicide XRD-498 caused severe interactions with enhanced injury to corn and wheat. That injury was corrected to varying degrees by the antidotes. COUNTER 15G/XRD-498 negative synergy was also seen with cotton, grain sorghum and rice.

Other tests of the invention were conducted with respect to various modes of application of the components of the invention, viz., herbicide/biocide/antidote. Crop seeds, e.g., were coated with various safeners and contacted with COUNTER 15G and herbicides. Other PPI, POE and in-furrow tests were conducted and in all these areas, negative synergy was observed and safening effected, both to varying degrees depending upon the system components.

As will be apparent, the data in the above tables reflect the fact that interactions between insecticides and herbicides are susceptible to having their phytotoxicity to crops reduced by antidotal (safener) compounds, while still providing control or suppression of weeds. The data also reflect the common occurrence that the safening effect on various herbicides by safeners will have different degrees of effect depending upon a variety of factors, including, relative concentrations of herbicides and/or co-herbicides and/or antidotes, weather and soil conditions, water content, etc., as well appreciated in the art.

The herbicidal compositions of this invention, including concentrates which require dilution prior t application, may contain at least one active ingredient and an adjuvant in liquid r solid form. The

1.0-15 parts) of dispersant and from 5 t about 95 parts (preferably 5-50 parts) of inert solid extender, all parts being by weight of the total composition. Where required, from about 0.1 to 2.0 parts of the solid inert extender can be replaced by a corrosion inhibitor or anti-foaming agent or both.

Other formulations include dust concentrates comprising from 0.1 to 60% by weight of the active ingredient on a suitable extender; these dusts may be diluted for application at concentrations within the range of from about 0.1-10% by weight.

Aqueous suspensions or emulsions may be prepared by stirring a nonaqueous solution of a water-insoluble active ingredient and an emulsification agent with water until uniform and then homogenizing to give stable emulsion of very finely divided particles. The resulting concentrated aqueous suspension is characterized by its extremely small particle size, so that when diluted and sprayed, coverage is very uniform. Suitable concentrations of these formulations contain from about 0.1-60%, preferably 5-50% by weight of active ingredient, the upper limit being determined by the solubility limit of active ingredient in the solvent. Concentrates are usually solutions of active ingredient in water-immiscible or partially water-immiscible solvents together with a surface active agent. Suitable solvents for the active ingredient of this invention include dimethylformamide, dimethylsulfoxide, N-methylpyrrolidone, hydrocarbons, and water-immiscible ethers, esters, or ketones. However, other high strength liquid concentrates may be formulated by dissolving the active ingredient in a solvent then diluting, e.g., with kerosene, to spray concentration.

The concentrate compositions herein generally contain from about 0.1 to 95 parts (preferably 5-60 parts) active ingr dient, about 0.25 to 50 parts (pr f rably 1-25 parts) surface active agent and where

required about 5 to 94 parts solvent, all parts being be weight based on the total weight of emulsifiable oil.

Granules are physically stable particulate compositions comprising active ingredient adhering to or distributed through a basic matrix of an inert, finely-divided particulate extender. In order to aid leaching of the active ingredient from the particulate extender, a surface active agent can be present in the composition. Natural clays, pyrophyllites, illite, and vermiculite are examples of operable classes of particulate mineral extenders. The preferred extenders are the porous, absorptive, preformed particles such as preformed and screened particulate attapulgite or heat expanded, particulate vermiculite and the finely-divided clays such as kaolin clays, hydrated attapulgite or bentonitic clays. These extenders are sprayed or blended with the active ingredient to form the herbicidal granules.

The granular compositions of this invention may contain from about 0.1 to about 30 parts by weight of active ingredient per 100 parts by weight of clay and 0 to about 5 parts by weight of surface active agent per 100 parts by weight of particulate clay.

The compositions of this invention can also contain other additaments, for example, fertilizers, other herbicides, other pesticides, safeners and the like used as adjuvants or in combination with any of the above-described adjuvants. Chemicals useful in combination with the active ingredients of this invention included, for example, triazines, ureas, sulfonylureas, carbamates, acetamides, acetanilides, uracils, acetic acid or phenol derivatives, thiolcarbamates, triazoles, benzoic acid and its derivatives, nitriles, biphenyl ethers, nitrobenzenes, etc.

Fertilizers useful in combination with the active ingredients include, for exampl , ammonium nitrate, urea, potash and superphosphate. Other useful

walnut flour, chalk, tobacco dust, charcoal, and the like. Typical liquid diluents include Stoddard's solvent, acetone, methylene chloride, alcohols, glycols, ethyl acetate, benzene, and the like. Liquids and wettable powders usually contain as a conditioning agent one or more surface-active agents in amounts sufficient to make a composition readily dispersible in water or in oil. The term "surface-active agent" includes wetting agents, dispersing agents, suspending agents, and emulsifying agents. Typical surface-active agents are mentioned in U.S. Patent No. 2,547,724.

Compositions of this invention generally may contain from about 5 to 95 parts herbicide-insecticide-and-antidote, about 1 to 50 parts surface-active agent, and about 4 to 94 parts solvent, all parts being by weight based on the total weight of the composition.

The crop may be protected by treating the crop seed with an effective amount of antidote prior to planting. Generally, smaller amounts of antidote are required to treat such seeds. A weight ratio of as little as 0.6 parts of antidote per 1000 parts of seed may be effective. The amount of antidote utilized in treating the seed may be increased if desired. Generally, however, a weight ratio of antidote-to-seed weight may range from 0.1 to 10.0 parts of antidote per 1000 parts of seed. Since only a very small amount of active antidote is usually required for the seed treatment, the compound preferably is formulated as an organic solution, powder, emulsifiable concentrate, water solution, or flowable formulation, which can be diluted with water by the seed treater for use in seed treating apparatus. Under certain conditions, it may be desirable to dissolve the antidote in an organic solvent or carrier for use as a seed treatment or the pure compound alon may be used under properly c ntrolled c nditions.

including, inter alia, numerous preferred dichloroacetamide antidote as representative of the compounds according to Formulae V and VI. It is to be understood that other compounds within the scope of the above formulae and other chemical classes are specifically contemplated as within the scope of this invention either as the herbicidal component or as a co-herbicide. For example, other triazolopyrimidine - and imidazolopyrimidine sulfonamides and their derivatives contemplated herein include the compounds described in the following U.S. patents and EP applications as relevant to the compounds of Formula I:

A. Compounds wherein R is the $-SO_2N(R_6)(R_7)$ moiety, A and B are both N and

1. R_1 and R_2 are discrete, uncombined radicals:

4,889,553
4,959,094

2. R_1 and R_2 are combined to form substituted and/or unsubstituted bivalent radicals which may contain one or more hetero atoms and saturated, partially saturated or unsaturated bonds:

4,740,233   4,854,964
4,741,764   4,960,455
4,755,212   4,859,231
4,818,273   4,795,483
4,886,883   4,910,306
4,954,163   4,959,473
4,979,981,   5,013,351,
5,041,157,   AU Appln. AU-A-68391,
EP Appln. 0 375 076, EP Appln 0 343 752

B. Compounds analogous to those in A2 above, except that in Formula I only one of A or B is N while the other is CR_3 as defined above:

4,731,446
4,799,952
4,892,576

propionate, N-(2'-phenoxy thyl)-2-[5'-(2"-chloro-4"-trifluoromethylphenoxy)-phenoxy]-propionamide, 2-methoxyethyl 2-[nitro-5-(2-chloro-4-trifluoromethyl-phenoxy)-phenoxyl-propionate and 2-chloro-4-tri-fluoromethylphenyl 3'-oxazolin-2'-yl-4'-nitrophenyl-ether.

Another generic class of agrichemically-important herbicidal compounds specifically contemplated for use as co-herbicidal compounds in combination with the antidotal compounds of this invention are the urea derivatives. Important herbicidal ureas include 1-(benzothiazol-2-yl)-1,3-dimethylurea; phenylureas, for example: 3-(3-chloro-p-tolyl)-1,1-dimethylurea ("chloro-toluron"), 1,1-dimethyl-3-(α,α,α-trifluoro-m-tolyl)urea ("fluometuron"), 3-(4-bromo-3-chlorophenyl)-methoxy-1-methylurea ("chlorbromuron"), 3-(4-bromophenyl)-1-methoxy-1-methylurea ("metobro- muron"), 3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea ("linuron"), 3-(4-chlorophenyl)-1-methoxy-1-methylurea ("monolinuron"), 3-(3,4-dichlorophenyl)-1,1-dimethyl-lurea ("diuron"), 3-(4-chlorophenyl)-1,1-dimethylurea ("monuron") and 3-(3-chloro-4-methoxyphenyl)-1,1-dimethylurea ("metoxuron");

Important herbicidal sulfonylureas and sulfonamides specifically contemplated as useful as the herbicidal component herein and/or a co-herbicides in compositions with the antidotal compounds of this invention include those disclosed in the following patents: U.S. Patent Numbers 4,383,113, 4,127,405, 4,238,621, 4,432,245, 4,443,243, 4,478,635, 4,537,619, 4,479,821, 4,481,029, 4,514,212, 4,548,638, 4,420,325, 4,638,004, 4,675,046, 4,681,620, 4,741,760, 4,723,123, 4,411,690, 4,718,937, 4,620,868, 4,668,277, 4,592,776, 4,666,508, 4,670,559, 4,671,819, 4,696,695, 4,731,446, 4,744,814, 4,678,498, 4,759,791, 4,786,314, 4,786,734, 4,889,550, 4,931,081 and 4,668,279; EP Numbers 084224, 173312, 87780, 190105, 256396, 264021, 264672, 142152,

Still other classes of herbicidal c mpounds contemplated for combination with th herbicidal and insecticidal components and with the antidotes of this invention include the following representative species:

Triazines and triazinones: 2,4-bis-(isopropylamino)-6-methylthio-1,3,5-triazine ("prometryn"), 2,4-bis-(ethylamino)-6-methylthio-1,3,5-triazine ("simetryn"), 2-(1',2'-dimethylpropylamino)-4-ethylamino-6-methylthio-1,3,5-triazine ("dimethametryn"), 2-(chloro-4,6-bis-(ethylamino)-1,3,5-triazine ("simazine"), 2-tert-butylamino-4-chloro-6-ethylamino-1,3,5-triazine ("terbuthylazine"), 2-tert-butylamino-4-ethylamino-6-methoxy-1,3,5-triazine ("terbumeton"), 2-tertbutylamino-4-ethylamino-6-methylthio-1,3,5-triazine ("terbutryn"), 2-ethylamino-4-isopropylamino-6-methylthio-1,3,5-triazine ("ametryn") and 3,4-bis-(methylamino)-6-tert-butyl-4,4-dihydro-1,2,-4-triazin-5-one.

Oxadiazolones: 5-tert-butyl-3-(2',4'-dichloro-5'-isopropoxyphenyl)-1,3,4-oxadiazol-2-one ("Oxadiazon").

Phosphates: S-2-methylpiperidinocarbonylmethyl O,O-dipropyl phosphorodithioate ("Piperophos").

Pyrazoles: 1,3-dimethyl-4-(2',4'-dichlorobenzolyl)-5-(4'-tolylsulfonyloxy)-pyrazole; aryl- and heterocyclic-substituted pyrazoles, e.g., as exemplified in EP No. 0361114; Japanese Kokai No. JP 50137061 and U.S. Patent 4,008,249.

In addition to the antid tal comp unds exemplified herein, other representative antidotal compounds according to Formula V or other structure which are contemplated for use with one or more herbicides or co-herbicides disclosed herein are expressly disclosed in various patents, e.g., U.S. Patent Nos. 3,959,304, 4,072,688, 4,137,070, 4,124,372, 4,124,376, 4,483,706, 4,636,244, 4,033,756, 4,493,726, 4,708,735, 4,256,481, 4,199,506, 4,251,261, 4,070,389, 4,231,783, 4,269,775, 4,152,137, 4,755,218, 4,933,166, 4,954,161, 4,964,893, 4,623,727, 4,822,884, 4,851,031, 4,902,340, 4,749,406, 4,758,264, 4,785,105, 4,785,106 4,294,764, 5,028,256, 5,037,256, 5,041,157 and EP Patent Application Nos. 159,287, 159,290, 258,184, 94,349, 2,121,403, 0253291, 0007588, 0190105, 0229649, 312762, 312763, 0430004 and 16618; PCT Patent Application Nos. WO 91/07874 and WO 91/08202; W. German Patent Application Nos. 28 28 222, 28 28 293.1, and 29 30 450.5, South African Patent No. 82/7681 and PRC Application No. 102 879-87.

Other antidotal compounds contemplated as suitable herein include 1-(5-chloro-isoquinon-8-yloxy)-1-methylhexyl acetate (Code No. CGA-185072), a safener for CGA-184927 herbicide in wheat, and 3-[(2,4-dichlorophenyl]2-(trichloromethyl)-5-(ethoxycarbonyl)-triazol-3-yl (Code No. HOE 70541), a safener also for use in wheat.

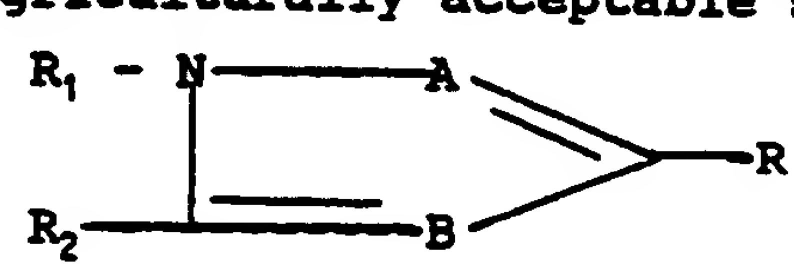
Although this invention has been described with respect to specific embodiments, the details of these embodiments are not to be construed as limitations. Various equivalents, changes and modifications may be made without departing from the spirit and scope of this invention, and it is understood that such equivalent embodiments are part of this invention.

O-[1,3-Dioxolan-2-ylmethyl]-2,2,2-trifluoromethyl-4'-chloroacetophenone oxime,
Benzenemethamine, N-[4-(dichloromethylene]-1,3-dithiolan-2-ylidene]-α-methyl, hydrochloride,
Diphenylmethoxy acetic acid, methyl ester,
1,8-Naphthalic anhydride,
4,6-Dichloro-2-phenyl-pyrimidine,
2-Chloro-N-[1-(2,4,6-trimethylphenyl)-ethenyl]acetamide,
Ethylene glycol acetal of 1,1-dichloroacetone,
1,3-Dioxolane, 2-(dichloromethyl)-2-methyl-,
5-Thiazolecarboxylic acid, 2-chloro-4-(trifluoromethyl)-, (phenylmethyl)-ester,
Phosphorothioic acid, O,O-diethyl O-(3-methylphenyl)ester,
4-Pentenenitrile, 2-methyl-2-[(4-methylphenyl)thio]-,
5-Chloro-8-(cyanomethoxy)quinoline,
1-Methylhexyl-2-(5-chloro-8-quinolinoxy)-acetate or
O-(Methoxycarbonyl)-2-(8-quinolinoxy)-acetamide oxime or

(c) Any of the compounds identified herein as Antidote Nos. 11, 29-33 and 42-80.

6. Composition according to Claim 5 wherein said herbicidal component (a) is a compound according to Formula I or agriculturally-acceptable salts thereof:

I



wherein

A and B are independently N or CR_3, provided that at least one of A or B is N;

is 1-3 and K is halogen; phenoxy- carbonyl, phenoxythiocarbonyl, aminocarbonyl, or where not self-inclusive said R_4 and R_6 members substituted with halogen, CN, CF_3, NO_2, OH and/or C_{1-10} alkyl, haloalkyl, alkoxy, alkoxyalkoxy, hydroxyalkoxy, alkylthioalkoxy, alkoxycarbonyl, or polyalkoxycarbonyl, phenyl, halophenyl, benzyl, benzyloxy, phenoxyalkoxy and agriculturally-acceptable salts thereof when R_4 and R_6 are H and

R_5 and R_7 are independently an aromatic hydrocarbon or heterocyclic radical having up to 10 ring members of which up to four may be N, O and/or S in the heterocyclic radical and said R_5 and R_7 members substituted with one or more R_4 members, 2-pyridyl, 2-pyridyloxy or 2-pyridylmethoxycarbonyl, dialkylaminoalkoxycarbonyl having up to 10 carbon atoms and the radical $C(O)ON = C(R_9)_2$, wherein R_9 is H, phenyl, phenylcarbonyl, benzyl, C_{1-10} alkyl, alkoxy, mono- or di-C_{1-6} alkylamino or -alkylaminocarbonyl, $-S(O)_nR_{10}$, where n is 0, 1, 2 or 3 and R_{10} is C_{1-6} alkyl, haloalkyl, mono- or di-C_{1-4} alkylamino or alkylcarbonyl, said compound of Formula I being used alone or in admixture with other known herbicidal compounds as co-herbicides.

7. Composition according to Claim 6 wherein said compounds according to Formula I are those wherein A and B are both nitrogen; R is $-SO_2N(R_6)(R_7)$; R_1 is phenyl, pyrimidinyl, triazinyl, thiadiazolyl, pyrazinyl, pyridinyl, or any of said R_1 radicals substituted with cyano, halogen, amino, mono- or di-C_{1-4} alkylamino, C_{1-6} alkyl, haloalkyl, alkylthio, alkoxy, alkoxyalkyl, alkoxycarbonyl, alkylthio, alkylsulfinyl or alkylsulfonyl; R_2 is hydrogen, halogen, cyano, amino, mono- or di-C_{1-4} alkylamino, C_{1-6} alkyl, alkylsulfinyl, alkylsulfonyl, alkoxy, alkoxyalkyl, alkoxycarbonyl, acyl, acyloxy or pyrrolyl optionally substituted with C_{1-4} alkyl; R_6 is hydrogen, C_{1-4} alkyl, acyl, alkylsulfonyl, alkoxy, alkoxycarbonyl, dialkylcarbamoyl or benzyl and R_7 is furyl, thiophene or phenyl or those radicals

9. Composition according to Claim 6 wherein in Formula I, A and B are both nitrogen N, R is $-SO_2N(R_6)(R_7)$ and R_1 and R_2 are combined to form one of the following divalent radicals:

(a) $$- N = \overset{Z}{\overset{|}{C}} - \overset{Y}{\overset{|}{C}} = \overset{X}{\overset{|}{C}} -$$

(b) $$- NH - \overset{Z}{\overset{|}{CH}} - \overset{Y}{\overset{|}{CH}} - \overset{X}{\overset{|}{CH}} -$$

(c) $$- NH - \overset{Z}{\overset{|}{C}} = \overset{Y}{\overset{|}{C}} - \overset{X}{\overset{|}{CH}} -$$

(d) $$- N = \overset{Z}{\overset{|}{C}} - \overset{Y}{\overset{|}{CH}} - \overset{X}{\overset{|}{CH}} -$$

(e) $$- \overset{Z}{\overset{|}{C}} = \overset{Y}{\overset{|}{C}} - N = \overset{X}{\overset{|}{C}} -$$

(f) $$- N = \overset{Y}{\overset{|}{C}} - \overset{X}{\overset{|}{N}} - \overset{D}{\overset{\|}{C}} -$$

(g) $$- S - \overset{Y}{\overset{|}{C}} = \overset{X}{\overset{|}{C}} -$$

wherein R_6 and R_7 are as defined above and X, Y and Z are independently an R_4 member, SO_2, or adjacent X and Y or Y and Z members may be combined to form a saturated, partially unsaturated or unsaturated homocyclic ring or heterocyclic ring containing up to 10 ring members of which up to 4 may be oxygen, sulfur and/or N and D is oxygen or sulfur.

10. Composition according t Claim 9 wherein R_1 and R_2 are combined to form the dival nt radical (a) .

Methyl-3-methyl-N-(5,7-dimethyl-1,2,4-triazolo-[1,5-a]-pyrimidine-2-sulfonyl)anthranilate;

Methyl-3-methyl-N-(5-methyl-7-ethoxy-1,2,-triazolo-[1,5-a]-pyrimidine-2-sulfonyl)-anthranilate;

Isopropyl-3-methyl-N-(5-methyl-1,2,4-triazolo-[1,5-a]-pyrimidine-2-sulfonyl)anthranilate;

6-Methyl-N-(2-bromo-6-methylphenyl)-1,2,4-triazolo-[1,5-a]-pyrimidine-2-sulfonamide;

6-Methyl-N-(2-fluoro-6-chlorophenyl)-1,2,4-triazolo-[1,5-a]-pyrimidine-2-sulfonamide;

6-Methyl-N-(2-chloro-6-methylphenyl)-1,2,4-triazolo[1,5-a]-pyrimidine-2-sulfonamide;

6-Methyl-N-(2-methyl-6-nitrophenyl)-1,2,4-triazolo-[1,5-a]-pyrimidine-2-sulfonamide;

7-Ethoxy-5-methyl-N-(2-trifluoromethylphenyl)-1,2,4-triazolo-[1,5-a]-pyrimidine-2-sulfonamide;

7-Methoxy-5-methyl-N-(2,6-dichloro-3-methylphenyl)-1,2,4-triazolo-[1,5-a]-pyrimidine-2-sulfonamide;

7-Ethoxy-5-methyl-N-(2-bromo-6-chloro-3-methylphenyl)-1,2,4-triazolo-[1,5-a]-pyrimidine-2-sulfonamide;

5,7-Dimethoxy-N-(2,6-dibromo-3-methylphenyl)-1,2,4-triazolo-[1,5-a]-pyrimidine-2-sulfonamide;

5,7-Dimethoxy-N-(2,6-dichlorophenyl)-1,2,4-triazolo-[1,5-a]-pyrimidine-2-sulfonamide;

7-Methyl-N-(2,6-dichlorophenyl)-1,2,4-triazolo-[1,5-a]-pyrimidine-2-sulfonamide;

N-(2,6-Dichlorophenyl)-1,2,4-triazolo-[1,5-a]-pyrimidine-2-sulfonamide;

7-Ethoxy-5-methyl-N-(2,6-dibromo-3-methylphenyl)-1,2,4-triazolo-[1,5-a]-pyrimidine-2-sulfonamide;

6-Chloro-N-(2,6-difluorophenyl)-1,2,4-triazolo-[1,5-a]-pyrimidine-2-sulfonamide;

5,7-Dim thyl-2-(N-[2-chl r -6-(2-hydroxyeth xy)-phenyl]-sulphamoyl)-1,2,4-triazolo[1,5-a]-pyrimidine;

5,7-Dimethyl-2-(N-[2-2-ethoxyethoxy)-6-fluoro-phenyl]-sulphamoyl)-1,2,4-triazolo[1,5-a]-pyrimidine;

5,7-Dimethyl-2-(N-[2-fluoro-6-(2-methylthio-ethoxy)-phenyl]-sulphamoyl)-1,2,4-triazolo-[1,5-a]-pyrimidine;

5,7-Dimethyl-2-(N-[2-chloro-6-(2-phenoxyethoxy)-phenyl]sulphamoyl)-1,2,4-triazolo[1,5-a]-pyrimidine;

5,7-Dimethyl-2-(N-[2-chloro-6-(2-methoxyethoxy)-phenyl]-sulphamoyl-1,2,4-triazolo-[1,5-a]-pyrimidine;

5,7-Dimethyl-2-(N-[2-chloro-6-(2-n-propoxyethoxy)-phenyl]-sulphamoyl)-1,2,4-triazolo[1,5-a]-pyrimidine;

5,7-Dimethyl-2-(N-[2-chloro-6-(3-methoxy-n-propoxy)phenyl]-sulphamoyl)-1,2,4-triazolo-[1,5-a]-pyrimidine;

5,7-Dimethyl-2-(N-[2-chloro-6-(2-isopropoxy)-ethoxyphenyl]-sulphamoyl)-1,2,4-triazolo-[1,5-a]-pyrimidine;

5,7-Dimethyl-(N-[2-fluoro-6-(2-n-propoxyethoxy)-phenyl]-sulphamoyl)-1,2,4-triazolo-[1,5-a]-pyrimidine;

5,7-Dimethyl-2-(N-[2-(2-ethoxyethoxy)phenyl]-sulphamoyl)-1,2,4-triazolo-[1,5-a]-pyrimidine;

5,7-Dimethyl-2-(N-[2,6-di(2-ethoxyethoxy)phenyl]-sulphamoyl)-1,2,4-triazolo-[1,5-a]-pyrimidine;

5,7-Dimethyl-2-(N-[2-2-ethoxyethoxy)-6-methoxy-phenyl]-sulphamoyl)-1,2,4-triazolo[1,5-a]-pyrimidine;

5,7-Dimethyl)-2-(N-[2-chloro-6-tetrahydr furfur-2-yl- xyphenyl]-sulphamoyl)-1,2,4-triazolo-[1,5-a]-pyrimidine;

Y is H, CN, halogen, C_{1-4} alkyl, haloalkyl or alkoxy;

R_3 is halogen, NO_2, CN, C_{1-4} alkyl, haloalkyl, C(O)alkyl or C(O)alkoxy;

R_6 is H, benzyl, C(O)C_{1-4}alkyl or -haloalkyl and agriculturally-acceptable salts thereof when R_6 is H and

R_7 is phenyl substituted in at least one ortho position with halogen, CN, NO_2, C_{1-4} alkyl, haloalkyl or $S(O)_{1-3}$alkyl or haloalkyl; amino, mono- or di-C_{1-4}alkylamino, optionally substituted phenyl, phenylthio, phenoxy or benzyl, wherein said substituents are from 1 to 4 of halogen, NO_2, CF_3, CN or C_{1-3} alkyl, preferably methyl; and at least one of the meta positions of the R_7 phenyl group is substituted with a C_{1-3} alkyl, preferably methyl.

13. Composition according to Claim 12 wherein said compound of Formula I is

N-(2,6-difluorophenyl)-4,6-dimethylimidazolo[1,2-a]-pyrimidine-2-sulfonamide;

N-(2,6-difluorophenyl)-3-chloro-4,6-dimethylimidazolo[1,2-a]-pyrimidine-2-sulfonamide;

N-(2,6-difluorophenyl)-3-bromo-4,6-dimethylimidazolo[1,2-a]-pyrimidine-2-sulfonamide;

N-(2,6-difluorophenyl)-3-methylthio-4,6-dimethylimidazolo[1,2-a]-pyrimidine-2-sulfonamide;

N-(2,6-dichlorophenyl)-4,6-dimethylimidazolo[1,2-a]-pyrimidine-2-sulfonamide;

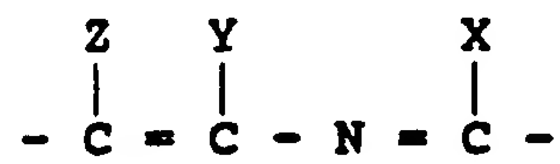
N-(2,6-difluorophenyl)-3-cyano-4,6-dimethylimidazolo[1,2-a]-pyrimidine-2-sulfonamide;

N-(2,6-difluorophenyl)-N-benzyl-3-chloro-4,6-dimethylimidazolo[1,2-a]-pyrimidine-2-sulfonamide;

N-(2-trifluoromethylphenyl)-4,6-dimethylimidazolo[1,2-a]-pyrimidine-2-sulfonamide;

N-(2-trifluor methylphenyl)-3-chloro-4,6-dimethylimidazolo[1,2-a]-pyrimidine-2-sulfonamide;

15. Composition according to Claim 9 wherein in Formula I R_1 and R_2 combine to form the divalent radical (e)

(e) 

wherein

X is H, CF_3, C_{1-4} alkyl, alkylthio or alkoxy;

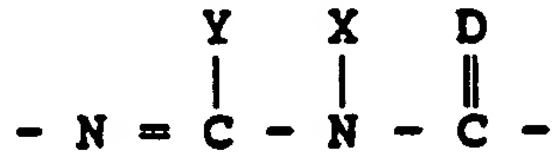
Y and Z are independently H, CF_3, CF_3, halogen or C_{1-4} alkoxy; provided that at least one of X, Y or Z is C_{1-4} alkoxy;

R_6 is H or C(O)C_{1-4} alkyl or -haloalkyl and agriculturally-acceptable salts thereof when R_6 is H and

R_7 is phenyl substituted in at least one ortho position with halogen, CN, NO_2, C_{1-4} alkyl, haloalkyl or $S(O)_{1-3}$ alkyl or haloalkyl; amino, mono- or di-C_{1-4} alkylamino, optionally-substituted phenyl, phenylthio, phenoxy or benzyl, wherein said substituents are from 1 to 4 of halogen, NO_2, CF_3, CN or C_{1-3} alkyl, preferably methyl; and at least one of the meta positions of the R_7 phenyl group is substituted with a C_{1-3} alkyl, preferably methyl.

16. Composition according to Claim 15 wherein said compound of Formula I is 5-methyl-N-(2,6-difluorophenyl)-1,2,4-triazolo[1,5a]-pyrimidine-2-sulfonamide.

17. Composition according to Claim 9 wherein in Formula I R_1 and R_2 are combined to form divalent radical (f)

(f) 

wherein D is oxygen or sulfur;

X and Y are independently H, alkyl, alkenyl or alkynyl having up to 6 carbon atoms, phenyl, phenylalkyl, phenylalkenyl, phenylalkynyl or where n t

N-(2,6-dichlor phenyl)-6,7-dihydro-5,6-dimethyl-7-thioxo-[1,2,4]triazolo[1,5-a]-[1,3,5]-triazine-2-sulphonamide;

N-(2,6-Dichlorophenyl)-6,7-dihydro-5,6-dimethyl-7-thioxo[1,2,4]triazolo[1,5-a][1,3,5]-triazine-2-sulphonamide;

N-(2,6-Dichloro-3-methylphenyl)-6,7-dihydro-5,6-dimethyl-7-thioxo-[1,2,4]triazolo[1,5-a][1,3,5]-triazine-2-sulphonamide;

6,7-Dihydro-5,6-dimethyl-N-(2-methyl-6-nitrophenyl)-7-thioxo-[1,2,4]triazolo-[1,5-a]-[1,3,5]-triazine-2-sulphonamide;

N-(2-Chloro-6-fluorophenyl)-6,7-dihydro-5,6-dimethyl-7-thioxo-[1,2,4]triazolo[1,5-a][1,3,5]-triazine-2-sulphonamide;

N-(2,6-Difluorophenyl)-6,7-dihydro-5,6-dimethyl-7-thioxo-[1,2,4]triazolo[1,5-a][1,3,5]-triazine-2-sulphonamide;

N-(2,6-Dibromophenyl)-6,7-dihydro-5,6-dimethyl-7-thioxo-[1,2,4]triazolo[1,5-a]-[1,3,5]-triazine-2-sulphonamide;

6,7-Dihydro-5,6-dimethyl-7-thioxo-N-(2-trifluoromethylphenyl)-[1,2,4]triazolo-[1,5-a]-[1,3,5]-triazine-2-sulphonamide;

6,7-Dihydro-5,6-dimethyl-N-phenyl-7-thioxo-[1,2,4]-triazolo[1,5-a]-[1,3,5]-triazine-2-sulphonamide;

N-(2-Chlorophenyl)-6,7-dihydro-5,6-dimethyl-7-thioxo-[1,2,4]triazolo-[1,5-a]-[1,3,5]-triazine-2-sulfonamide.

20. Composition according to Claim 6 wherein in Formula I A is N, B is CR_3, R_1 and R_2 are combined to form divalent radical (f)

(f) $$-N=\overset{\overset{Y}{|}}{C}-\overset{\overset{X}{|}}{N}-\overset{\overset{D}{\|}}{C}-$$

D is oxygen or sulfur;

22. Compositi n acc rding to Claim 21 wherein said compound of Formula I is

N-(2,6-Dichlorophenyl)-6,7-dihydro-5,6-dimethyl-3-methoxycarbonyl-7-oxo-pyrazolo[1,5-a]-[1,3,5]-triazine-2-sulphonamide;

N-(2,6-Difluorophenyl)-6,7-dihydro-5,6-dimethyl-3-methoxycarbonyl-7-thioxo-pyrazolo[1,5-a]-[1,3,5]-triazine-2-sulphonamide;

N-(2,6-Difluorophenyl)-6,7-dihydro-5,6-dimethyl-3-methoxycarbonyl-7-oxo-pyrazolo[1,5-a]-[1,3,5]-triazine-2-sulphonamide;

N-(2,6-Dichlorophenyl)-6,7-dihydro-5,6-dimethyl-3-methoxycarbonyl-7-thioxopyrazolo[1,5-a]-[1,3,5]-triazine-2-sulphonamide;

N-(2,6-Dichloro-3-methylphenyl)-6,7-dihydro-5,6-dimethyl-3-methoxycarbonyl-7-oxopyrazolo[1,5-a]-[1,3,5]-triazine-2-sulphonamide;

N-(2,6-Dichloro-3-methylphenyl)-6,7-dihydro-5,6-dimethyl-3-methoxycarbonyl-7-thioxopyrazolo-[1,5-a]-[1,3,5]-triazine-2-sulphonamide;

N-(2-Chloro-6-fluorophenyl)-6,7-dihydro-5,6-dimethyl-3-methoxycarbonyl-7-oxopyrazolo-[1,5-a][1,3,5]-triazine-2-sulphonamide;

N-(2-Chloro-6-fluorophenyl)-6,7-dihydro-5,6-dimethyl-3-methoxycarbonyl-7-thioxo-pyrazolo-[1,5-a][1,3,5]-triazine-2-sulphonamide;

N-(2-Chloro-6-methylphenyl)-6,7-dihydro-5,6-dimethyl-3-meth xycarbonyl-7-ox pyrazolo-[1,5-a][1,3,5]-triazin -2-sulph namide;

R_7 is an aromatic r heteroaromatic R_6 member.

24. Composition according to Claim 23 wherein X and Y are independently H or C_{1-6} alkyl; R_6 is H and R_7 is phenyl substituted with one or more halogen, NO_2, C_{1-4} alkyl, alkoxy, alkoxycarbonyl or alkylthio groups.

25. Composition according to Claim 24 wherein said compound of Formula I is N-(2,6-difluorophenyl)-thiazole[3,2-b][1,2,4]triazole-2-sulfonamide.

26. Composition according to Claim 6 where in Formula I R is $-N(R_4)SO_2R_5$; A and B are both N and R_4 and R_5 have the meanings defined.

27. Composition according to Claim 26 where in Formula I R_1 and R_2 are combined to form the above bivalent radical (a),

$$\text{(a)} \qquad -N=\overset{\overset{\displaystyle Z}{|}}{C}-\overset{\overset{\displaystyle Y}{|}}{C}=\overset{\overset{\displaystyle X}{|}}{C}-$$

or its tetrahydro analogs of bivalent radical (b)

$$\text{(b)} \qquad -NH-\overset{\overset{\displaystyle Z}{|}}{CH}-\overset{\overset{\displaystyle Y}{|}}{CH}-\overset{\overset{\displaystyle X}{|}}{CH}-$$

R_4 and R_5 are as defined and

X, Y and Z are independently an R_4 member, SO_2 or adjacent X and Y or Y and Z members may be combined to form a saturated, partially-saturated or unsaturated homocyclic or heterocyclic ring containing up to 10 ring members of which up to 4 may be O, S and/or N.

28. Composition according to Claim 27 wherein

Y and R_4 are H;

X and Z are H or C_{1-4} alkyl or alkoxy and

R_5 is phenyl substituted in a first ortho position with halogen, NO_2, CF_3, CN, carboxyl or C_{1-4} alkoxycarbonyl; in the other ortho position in H, halogen or C_{1-4} alkoxycarbonyl and in the meta position adjacent said first ortho position with H, halogen or C_{1-4} alkyl.

30. Comp sition according to Claim 26 wherein in Formula I R_1 and R_2 are combined to form the divalent radical (h)

$$(h) \qquad -N=\overset{\overset{\displaystyle Y}{|}}{C}-N=\overset{\overset{\displaystyle X}{|}}{C}-$$

R_4 and R_5 are as defined and
X and Y are independently an R_4 member or SO_2.

31. Composition according to Claim 30 wherein said compound of Formula I is

N-(5,7-dimethyl)-6,7-dihydro-[1,2,4]-triazole-[1,5-a][1,3,5]-triazine-2-(2,6-difluoro-phenyl)-sulfonamide;

N-(5-methyl)-6,7-dihydro-[1,2,4]-triazole[1,5-a]-[1,3,5]-triazine-2-(2,6-difluoro-phenyl)-sulfonamide;

N-(7-methoxy-6,7-dihydro-[1,2,4]-triazole[1,5-a]-[1,3,5]-triazine-2-(2,6-dichloro-phenyl)-sulfonamide;

N-(5,7-dimethoxy)-6,7-dihydro-[1,2,4]-triazole-[1,5-a][1,3,5]-triazine-2-(2,3,6-trimethylphenyl)sulfonamide;

N-(5-chloro)-6,7-dihydro-[1,2,4]-triazole[1,5-a]-[1,3,5]-triazine-2-(2-acetyl-6-methyl-phenyl)-sulfonamide or

N-(5-methoxymethyl)-6,7-dihydro[1,2,4]-triazole-[1,5-a][1,3,5]-triazine-2-(2,6-difluorophenyl)-sulfonamide.

32. Composition according to Claim 30 wherein in Formula I R_5 is a substituted pyrazolyl, furanyl or thiophenyl radical.

33. Composition according to Claim 32 wherein R_5 is pyrazol-4-yl (un)substituted in the 1-position with C_{1-4} alkyl or phenyl and in the 3- and 5- positions with H, halogen, CN, NO_2, CF_3, phenyl, benzyl, C_{1-4} alkyl, aminocarbonyl, mono- or dialkylaminocarbonyl, alk xycarbonyl, alkenyloxycarbonyl or alkynyloxy-

radicals substituted with halogen, amino, cyano, nitro, carbamoyl, C_{1-4} alkyl, alkoxy, dihaloalkoxy, alkoxy-carbonyl, mono- or dialkylamino, mono- or dialkylcar-bamoyl or $S(O)_p$-alkyl, -alkenyl or -alkynyl having up to 4 carbon atoms or where not self-inclusive said substi-tutable radicals substituted with another R_1 member and p is 0-4.

36. Composition according to Claim 35 wherein in sulfonylurea compounds according to Formula II:

R_{11} is a phenyl radical substituted in one position ortho to the $-SO_2$ radical with halogen, pre-ferably chloro, C_{1-3} alkoxycarbonyl, chloroalkoxy-carbonyl or alkoxyalkoxy; a 2-(C_{1-4} alkoxycarbonyl) thiophen-3-yl radical; a pyridin-2-yl radical substi-tuted in the 3-position with a C_{1-3} alkylsulfonyl or N,N-C_{1-3} dialkyl radical; pyrazol-3-yl, pyrazol-4-yl or pyrazol-5-yl radical or an imidazol-2-yl, imidazol-4-yl or imidazol-5-yl radical, said pyrazolyl- and imida-zolyl-radicals being substituted in the 1 position with H or a C_{1-8} alkyl, preferably C_{1-3} alkyl radical, and in the substitutable positions with H, halogen, preferably bromo or chloro, NO_2, C_{1-4} alkyl, alkoxy, mono- or dialkylamino, or dialkylaminosulfonyl, alkylsulfinyl, alkylsulfonyl, thioalkyl or alkoxycarbonyl radical and

R_{12} is a pyrimidin-2-yl or 1,3,5-triazin-2-yl radical independently substituted in the 4- and 6-positions, respectively, with C_{1-4} alkyl, preferably methyl, alkoxy, preferably methoxy, and/or difluoro-methoxy radicals.

37. Composition according to Claim 36 wherein said sulfonylurea compound is:

Benzenesulfonamide, 2-chloro-N-[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]-carbonyl];

Benzoic acid, 2-[[[[(4-chloro-6-methoxy-2-pyrimidin-2-yl)amino]carbonyl]amino]-sulfonyl]-ethyl ester;

N-[(4-methoxy-6-methylpyrimidin-2-yl)-aminocarbonyl]-1-(1-methylethyl)-1H-imidazole-2-sulfonamide;

N-[(4,6-dimethoxypyrimidin-2-yl)amino-carbonyl]-1-(1-methylethyl)-1H-imidazole-2-sulfonamide;

N-[(4,6-dimethylpyrimidin-2-yl)amino-carbonyl]-1-ethyl-1H-imidazole-2-sulfonamide;

N-[(4-methoxy-6-methylpyrimidin-2-yl)-aminocarbonyl]-1-ethyl-1H-imidazole-2-sulfonamide;

N-[(4,6-dimethoxypyrimidin-2-yl)amino-carbonyl]-1-ethyl-1H-imidazole-2-sulfonamide;

N-[(4,6-dimethoxypyrimidin-2-yl)amino-carbonyl]-5-bromo-1-methyl-1H-imidazole-4-sulfonamide.

38. Composition according to Claim 5 wherein said herbicidal component is an imidazolinone compound.

39. Composition according to Claim 38 wherein said imidazolinone compound is:

3-Quinolinecarboxylic acid, 2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-;

3-Pyridinecarboxylic acid, 2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-;

Benzoic Acid, 2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-4(or 5)-methyl;

3-pyridinecarboxylic acid, 5-ethyl-2-[4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-;

41. Composition acc rding to Claim 40 wherein said herbicidal compounds according to Formula III are those wherein the R_{13} member is an alkoxyalkyl radical of the structure -(E)-O-L, wherein E and L are linear or branched-chain alkyl residues having a combined total of up to 8 carbon atoms; or a substituted or unsubstituted C_{4-10} heterocyclyl or heterocyclylmethyl radical containing from 1 to 4 ring hetero atoms selected independently from N, S or O atoms and the R_{14} member is also one of said heterocyclyl or heterocyclylmethyl radicals or an optionally-substituted phenyl radical.

42. Composition according to Claim 40 wherein said R_{13} and/or R_{14} members of Formula III are independently, the furanyl, thienyl, pyrazolyl, pyrrolyl, isoxazolyl, isothiazolyl, triazolyl, imidazolyl, and pyrimidinyl radicals and their analogs having a methylene ($-CH_2-$) moiety connecting the heterocyclic radical to the acetamide nitrogen atom, or a heterocyclic radical attached directly to the amide nitrogen through a ring carbon atom or a ring hetero atom as appropriate; propynyl, alkoxycarbomethyl or -ethyl, alkoxyiminoalkyl, benzyl, hydroxyalkyl, haloalkoxy and -alkoxyalkyl, cyanoalkoxy and -alkoxyalkyl, methyl, ethyl, propyl, butyl or their isomers.

43. Composition according to Claim 42 wherein said compound of Formula III is N-(2,4-dimethylthien-3-yl)-N-(1-methoxyprop-2-yl)-2-chloroacetamide; N-(1H-pyrazol-1-ylmethyl)-N-(2,4-dimethylthien-3-yl)-2-chloroacetamide or N-(1-pyrazol-1-yl methyl)-N-(4,6-dimethoxypyrimidin-5-yl)-2-chloroacetamide.

44. Composition according to Claim 40 wherein said herbicidal component is an α-chloroac tanilide acc rding to Formula IV

2-chloro-N-(2,6-dimethyl-1-cycl hexen-1-yl)-N-(1H-pyrazol-1-yl-methyl)acetamide;
2-chloro-N-isopropyl-1-(3,5,5-trimethylcyclohexen-1-yl)acetamide
2-Chloro-2'-methyl-6'-methoxy-N-(isopropoxymethyl)acetanilide;
2-Chloro-2'-methyl-6'-trifluoromethyl-N-(ethoxymethyl)acetanilide;
N-(2,4-dimethylthien-3-yl)-N-(1-methoxyprop-2-yl)-2-chloroacetamide;
N-(1H-pyrazol-2-ylmethyl)-N-(2,4-dimethylthien-3-yl)-2-chloroacetamide and
N-(1-pyrazol-1-ylmethyl)-N-(4,6-dimethoxypyrimidin-5-yl)-2-chloroacetamide.

46. Composition according to Claim 45 wherein said herbicidal component according to Formula IV is 2-chloro-2'-ethyl-6'-methyl-N-(ethoxymethyl)-acetanilide, 2-chloro-2',6'-diethyl-N-(methoxymethyl)-acetanilide, 2-chloro-2',6'-diethyl-N-(butoxymethyl)-acetanilide, 2-chloro-2'-ethyl-6'-methyl-N-(1-methyl-2-methoxyethyl)-acetanilide, 2-chloro-2',6'-diethyl-N-(2-n-propoxyethyl)acetanilide or 2-chloro-2',6'-dimethyl-N-(pyrazolylmethyl)acetanilide.

47. Composition according to Claim 5 wherein said herbicidal component is a thiocarbamate compound.

48. Composition according to Claim 47 wherein said thiocarbamate compound is

<u>cis-/trans</u>-2,3-dichloroallyl-diisopropylthiolcarbamate;
Ethyl dipropylthiocarbamate;
S-ethyl diisobutyl(thiocarbamate);
S-propyl dipropyl(thiocarbamate);
2,3,3-trichloroallyl-diisopropylthiocarbamate.

Benzenemethamine, N-[4-(dichlor methylene]-1,3-dithiolan-2-ylidene]-α-methyl, hydrochloride,

Diphenylmethoxy acetic acid, methyl ester,

1,8-Naphthalic anhydride,

4,6-Dichloro-2-phenyl-pyrimidine,

2-Chloro-N-[1-(2,4,6-trimethylphenyl)-ethenyl]acetamide,

Ethylene glycol acetal of 1,1-dichloroacetone,

1,3-Dioxolane, 2-(dichloromethyl)-2-methyl-,

5-Thiazolecarboxylic acid, 2-chloro-4-(trifluoromethyl)-, (phenylmethyl)-ester,

Phosphorothioic acid, O,O-diethyl O-(3-methylphenyl)ester,

4-Pentenenitrile, 2-methyl-2-[(4-methyl-phenyl)thio]-,

5-Chloro-8-(cyanomethoxy)quinoline,

1-Methylhexyl-2-(5-chloro-8-quinolinoxy)-acetate or

O-(Methoxycarbonyl)-2-(8-quinolinoxy)-acetamide oxime or

(c) Any of the compounds identified herein as Antidote Nos. 11, 29-33 or 42-80.

54. Composition according to Claim 53 wherein in Formula V R_{17} is C_{1-3} haloalkyl, R_{18} and R_{19} are independently C_{2-4} alkenyl or haloalkenyl or 2,3-dioxolan-dioxolan-2-yl-methyl and R_{18} and R_{19} when combined form a C_{4-10} saturated or unsaturated heterocyclic ring containing O, S and/or N atoms and which may be substituted with C_{1-5} alkyl, haloalkyl, alkoxy, or alkoxyalkyl or haloacyl groups.

Oxazolidine, 3-(dichloroacetyl)-2,2-dimethyl-5-(2-furanyl)-,

Oxazolidine, 3-(dichloroacetyl)-2,2-dimethyl-5-(2-thienyl)-,

Pyridine, 3-[3-(dichloroacetyl)-2,2-dimethyl-5-oxazolidinyl]-,

4-(dichloroacetyl)-1-oxa-4-azaspiro-(4,5)-decane.

59. Composition according to Claim 53 wherein said compound according to Formula V is:

4-(Dichloroacetyl)-3,4-dihydro-3-methyl-2H-2,4-benzoxazine,

Ethanone, 2,2-dichloro-1-(1,2,3,4-tetrahydro-1-methyl-2-isoquinolinyl)-,

N-(Dichloroacetyl)-1,2,3,4-tetrahydroquinaldine,

1-(Dichloroacetyl)-1,2,3,4-tetrahydroquinoline,

Cis/trans-piperazine, 1,4-bis(dichloro 1,4-acetyl)-2,5-dimethyl-,

1,5-Diazacyclononane, 1,5bis-(dichloroacetyl,

1-Azaspiro[4,4]nonane, 1-(dichloroacetyl),

Pyrrolo[1,2-a]-pyrimidine-[6(2H)]-one, 1-(dichloroacetyl)hexahydro-3,3,8a-trimethyl,

2,2-Dimethyl-3-(dichloroacetyl)-1,3-oxazole and

2,2-Dimethyl-5-methoxy-3-(dichloroacetyl)-1,3-oxazole.

60. Composition according to Claim 53 wherein said antidotal compound is:

α-[(Cyanomethoxy)imino]benzeneacet nitrile,

α-[(1,3-Di xolan-2-yl-methoxy)imino]benzeneacetonitrile,

63. Comp siti n c mprising nic sulfur n, primisulfuron, DPX E9636, NC-311, NC-319 or acet chlor as the herbicidal component; phorate, terbufos or chlorpyrifos as the insecticidal component and MON-7400, MON-13900 or AD-67 as the antidotal component.

64. Method for combatting negative synergism in crops induced by the interaction of a herbicidal compound and a biocidal compound which comprises providing an antidotal compound in sufficient amount to reduce or inhibit said negative synergism.

65. Method according to Claim 64 wherein said herbicidal compound exhibits ALS or non-ALS inhibitory action in a plant.

66. Method according to Claim 65 wherein said herbicide is a sulfonylurea, imidazolinone, azolopyrimidine sulfonamide, α-haloacetamide or thiocarbamate compound.

67. Method according to Claim 66 wherein said biocide is an insecticide, fungicide or nematicide.

68. Method according to Claim 67 wherein said antidotal compound is

(a) a compound as defined herein for Formulae V or VI;

(b) any of the compounds

α-[(Cyanomethoxy)imino]benzeneaceto-nitrile,

α-[(1,3-Dioxolan-2-yl-methoxy)imino]-benzeneacetonitrile,

O-[1,3-Dioxolan-2-ylmethyl]-2,2,2-tri-fluoromethyl-4'-chloroacetophenone oxime,

Benzenemethamine, N-[4-(dichloromethylene]-1,3-dithiolan-2-ylidene]-α-methyl, hydrochloride,

Diphenylmethoxy acetic acid, methyl ester,

1,8-Naphthalic anhydride,

74. Method according to any f Claims 68-72 or 73 wherein said antidotal compound is a compound according to Formula V.

75. Method according to Claim 74 wherein said antidotal compound is dichlormid or PPG-1292.

76. Method according to any of Claims 68-72 or 73 wherein said antidotal compound according to Formula VI is

Oxazolidine, 3-(dichloroacetyl)-2,2,5-trimethyl-,

Oxazolidine, 3-(dichloroacetyl)-2,2-dimethyl-5-phenyl-,

Oxazolidine, 3-(dichloroacetyl)-2,2-dimethyl-5-(2-furanyl)-,

Oxazolidine, 3-(dichloroacetyl)-2,2-dimethyl-5-(2-thienyl)-,

Pyridine, 3-[3-(dichloroacetyl)-2,2-dimethyl-5-oxazolidinyl]-, or

4-(dichloroacetyl)-1-oxa-4-azaspiro-(4,5)-decane.

77. Method according to Claim 74 wherein said antidotal compound according to Formula V is:

4-(Dichloroacetyl)-3,4-dihydro-3-methyl-2H-2,4-benzoxazine,

Ethanone, 2,2-dichloro-1-(1,2,3,4-tetrahydro-1-methyl-2-isoquinolinyl)-,

N-(Dichloroacetyl)-1,2,3,4-tetrahydroquinaldine,

1-(Dichloroacetyl)-1,2,3,4-tetrahydroquinoline,

Cis/trans-piperazine, 1,4-bis(dichloro 1,4-acetyl)-2,5-dimethyl-,

1,5-Diazacyclononane, 1,5bis-(dichloroacetyl,

1-Azaspiro[4,4]nonane, 1-(dichloroacetyl),

Pyrrolo[1,2-a]-pyrimidine-[6(2H)]-one, 1-(dichloroac tyl)hexahydro-3,3,8a-trim thyl,

79. Method according to Claim 73 wherein said antidotal compound is any of Antidote Nos. 11 29-33 or 42-80 as defined herein.

80. Method for combatting negative synergism in crops induced by the interaction of the herbicide nicosulfuron, primisulfuron, DPX E9636, NC-311, NC-319, XRD-498 or acetochlor and the insecticide phorate, terbufos or chlorpyrifos, which comprises providing a sufficient amount of the antidotal compound dichlormid, R-29148, PPG-1292, AD-67, MON-7400 or MON-13900 to reduce or inhibit said negative synergism.

81. Method according to any of Claims 68-79 or 80 wherein said crops are corn, rice, barley, sorghum, wheat, cotton, soybeans and sugarbeets.

82. Method for combatting negative synergism in corn induced by the interaction of nicosulfuron, primisulfuron, DPX E9636, NC-311, NC-319, XRD-498 or acetochlor with phorate, terbufos or chlorpyrifos, which comprises providing a sufficient amount of dichlormid, R-29148, PPG-1292, AD-67, MON-7400 or MON-13900 to reduce or inhibit said negative synergism.

PCT/US 91/09783

International Application No

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	EP,A,0 312 763 (AMERICAN CYANAMID CO.) 26 April 1989 see page 2, line 5 - page 3, line 21 see page 4, line 6 - line 41; claims	1-4,38, 39,49-51
A	WO,A,8 906 492 (FMC CORP.) 27 July 1989 see page 2, line 12 - line 18 see page 7, line 10 - line 30; claims; tables 1-7	1,2
A	CH,A,651 445 (CIBA-GEIGY AG) 30 September 1985 see page 2, right column, line 37 - page 3, right column, line 50; claims; examples 2,3	1-5